

Material Progress in Water Splitting: A Comprehensive Review of Electrocatalyst Advances (2023–2025)

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Abstract

Electrochemical water splitting is central to green hydrogen production, offering a carbon-neutral way to store and deliver renewable energy. Over the past three years (2023-2025), the field has seen an unprecedented pace of materials development, profoundly shaping the design principles of electrocatalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). In this review, we critically assess key material breakthroughs across five disruptive categories: (i) MXene composites and heterostructure engineering; (ii) single-atom catalysts (SACs) with atomically coordinated active centers; (iii) high-entropy alloys and oxyhydroxides with multi-element synergies; (iv) transition metal phosphides, chalcogenides, and carbides with adjustable electronic states; and (v) novel materials and strategies for direct seawater electrolysis. For each category, we review synthetic approaches, structure-activity correlations, mechanistic insights from density functional theory (DFT) studies, and state-of-the-art electrochemical performance metrics, including overpotential, Tafel slope, turnover frequency (TOF), and stability. Particular attention is paid to advances that have enabled non-precious metal catalysts to match the performance of Pt and IrO₂ standards, as well as new challenges in high-current-density operation, membrane electrode assembly (MEA) integration, and selectivity in direct seawater splitting. The review culminates with an outlook on the most pressing challenges and the most promising materials design strategies to achieve scalable, practical green hydrogen production by 2030.

Keywords: Water Splitting, HER, OER, MXene, SAC, High-Entropy Alloys, Seawater Electrolysis, Transition Metal Phosphides

1. Introduction

Increasingly urgent climate change challenges propelled the position of hydrogen from a chemical commodity to the primary fuel for a fossil-fuel-free future. Green hydrogen, produced by the coupling of water splitting electrolysis and renewable electricity (e.g., solar, wind), offers a new possibility: it can be stored, transported and reconverted to electricity or heat with water being the sole by-product of combustion, thus decoupling energy generation from carbon emissions[1]. The installed capacity for electrolytic hydrogen production has soared since 2022, due to policy support in the European Union, the US, China, India and South Korea, which have all announced multi-billion-dollar investments in green hydrogen.[2]

The thermodynamics of water splitting was divided into two half electrochemical reactions: the hydrogen evolution reaction (HER) at the cathode, which reduces protons and electrons to produce H₂ ($2\text{H}^+ + 2\text{e}^- \rightarrow$

H_2 ; $E^\circ = 0 \text{ V}$ vs. RHE) and the oxygen evolution reaction (OER) at the anode, a more complicated four-electron process that oxidizes water to O_2 ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$; $E^\circ = +1.23 \text{ V}$ vs. RHE). The thermodynamic minimum cell voltage for overall water splitting was 1.23 V, but practical electrolyzer systems operate at 1.6–2.0 V due to kinetic overpotentials at both electrodes, ohmic resistance losses, and mass transport limitations [3]. Reducing these overpotentials and particularly the OER overpotential, which typically accounts for the majority of the efficiency loss was the central challenge in electrocatalyst materials design.

The best-performing catalysts are still based on the precious metals: platinum (Pt) for the HER and iridium oxide (IrO_2) or ruthenium oxide (RuO_2) for the OER. These are highly active but scarce and expensive metals - with worldwide Pt reserves of only ~16,000 tons and annual Ir production of less than 10 tons, which renders their use unsustainable on a large scale [4]. The need to replace such precious metals with earth-abundant non-precious-metal alternatives with the same performance has resulted in a veritable explosion in scientific research, especially since 2022.

The most fertile period was the past three years (2023-2025), which has witnessed major paradigm shifts: the use of MXene heterostructures as bifunctional catalyst supports; the advent of single-atom catalysis as a general approach to increase the atom-level efficiency; the rise of high-entropy materials that harness the multi-element configurational entropy to create unprecedented active-site diversity; the development of industrially rugged transition metal phosphides and chalcogenides; and, most importantly, the first successful demonstrations of practical direct seawater electrolysis with purposely designed corrosion-resistant catalysts. This review offers a comprehensive, critical overview of these developments, placing each in the context of the evolution of the field, while highlighting the most significant materials innovations of this era. Figure 1 below conceptually illustrates the water splitting reaction and the five material families reviewed in this work.

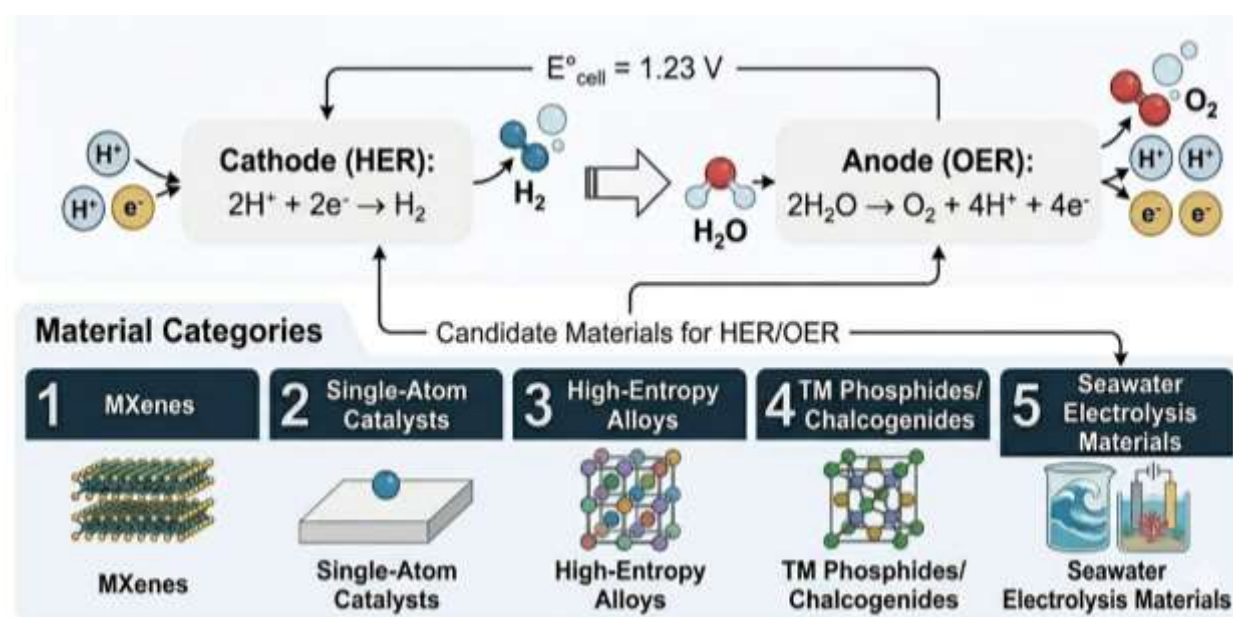


Figure 1. Schematic representation of overall electrochemical water splitting and the five principal electrocatalyst material families reviewed in this work. The thermodynamic cell voltage of 1.23 V is augmented by overpotentials (η) at both electrodes in practice.

2. Fundamentals of Electrocatalytic Water Splitting

2.1 Reaction Mechanisms and Key Metrics

The HER consists of two mechanisms in acid and alkaline media. In acidic conditions, the Volmer step ($\text{H}^+ + \text{e}^- \rightarrow \text{H}^*$) is followed either by the Heyrovsky step ($\text{H}^* + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2$) or the Tafel step ($\text{H}^* + \text{H}^* \rightarrow \text{H}_2$) (H^* is a hydrogen atom (H) that is attached (adsorbed) to the surface of a material (like Pt, MoS_2 , Ni, etc.)). The Tafel slope derived from polarization curves directly indicates the rate-determining step: $\sim 120 \text{ mVdec}^{-1}$ for Volmer-limited, $\sim 40 \text{ mVdec}^{-1}$ for Heyrovsky-limited, and $\sim 30 \text{ mVdec}^{-1}$ for Tafel-limited kinetics [5]. In alkaline media, an additional water dissociation step ($\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^* + \text{OH}^-$) precedes hydrogen adsorption, introducing an additional kinetic barrier that most non-precious HER catalysts struggle with [6].

The OER involves four sequential proton-coupled electron-transfer steps, producing adsorbed OH^* , O^* , and OOH^* intermediates before O_2 release. The key descriptor of OER activity is the free energy of the OOH^* intermediate relative to OH^* : the universal scaling relation between $\Delta G(\text{OOH}^*)$ and $\Delta G(\text{OH}^*)$, approximately 3.2 eV apart, defines a theoretical minimum overpotential of $\sim 0.37 \text{ V}$ even for an ideal catalyst. Breaking this scaling relation through site engineering is a central goal of modern OER catalyst design [7].

The most common performance metrics reported throughout this review are: (1) overpotential (η , in mV), measured at a nominal current density (10, 50 or 100 mA cm^{-2}); (2) Tafel slope (mV dec^{-1}), which is a measure of kinetic rate; (3) exchange current density (j_0); (4) turnover frequency (TOF, s^{-1}), which measures the per-site activity; (5) electrochemical active surface area (ECSA); (6) Faradaic efficiency; and (7) stability, usually measured by chronoamperometric or chrono potentiometric retention (100-1000 h). For industrial applications, operation at $\geq 500 \text{ mA cm}^{-2}$ is required, which is increasingly tested in recent reports.

2.2 Role of Materials Design Strategies

Over the past three years, a set of design strategies has emerged that were common to most of the progress described here. Defect engineering (vacancies, dislocations, amorphous phases) leads to under-coordinated metal atoms with shifted d-band centers and stronger binding of reaction intermediates [8]. Heterostructure engineering at nanoscale junctions creates built-in electric fields that promote charge transfer and affect the binding of reaction intermediates at the heterojunction [9]. Foreign atoms (metallic or non-metallic) modify the electronic structure of the active sites, often bringing catalysts closer to the top of the Bronsted-Evans-Polanyi volcano. Phase engineering, especially the conversion of semiconducting 2H phases of dichalcogenides to metallic 1T phases, leads to a significant change in conductivity and catalytic activity. Lastly, nano- and micro-scale morphology engineering increases active surface area and facilitates reactant/product transport.

3. MXene Electrocatalysts for Water Splitting

3.1 Properties and Overview of MXene

Since their emergence in 2011, MXene, a rapidly growing family of two-dimensional (2D) transition metal carbides, nitrides and carbonitrides with a general formula of $\text{M}_{n+1}\text{X}_n\text{T}_x$ (where M = an early transition metal, X = C and/or N, T = surface terminations, such as -O, -OH, -F) was proven most promising platforms for the development of electrocatalysts [10]. Their outstanding properties for electrocatalysis include: good electrical conductivity (as high as $20,000 \text{ S cm}^{-1}$ for $\text{Ti}_3\text{C}_2\text{T}_x$), inherent hydrophilicity for improved electrolyte wettability, large surface areas (up to $1200 \text{ m}^2 \text{ g}^{-1}$ for delaminated MXenes), abundant

surface functional groups that can serve as active sites for metal nanoparticles and single atoms, and excellent surface functionalizability [11].

Despite the above merits, inherently, MXenes' HER and OER activity was only moderate. This indicates that composite and heterostructure designs were required. The following three strategies were commonly used for engineering MXenes over the past two years (2023-2025): (i) compositing MXenes with transition metal phosphides to form bifunctional electrocatalysts; (ii) anchoring single atoms and small clusters on MXene surfaces to form single-atom/small cluster catalysts; and (iii) combining MXenes with metal chalcogenides or layered double hydroxides to form multi-functional heterostructures.

3.2 MXene-Transition Metal Phosphide Composites

Bifunctional NiCoP/Ti₃C₂T_x MXene was a popular choice for electrocatalysts. In a groundbreaking 2024 study, Niu et al. reported that a Pt-NiCoP/Ti₃C₂T_x catalyst by a Pt-NiCo alloy precursor deposited on MXene sheets was transformed into nanobowls through controlled phosphidation with just 1.0 mol% Pt. This structure exhibited an outstanding HER overpotential of merely 26.5 mV at 10 mA cm⁻² in alkaline electrolytes (close to the performance of pure Pt) and high stability [12]. The MXene surface enabled effective electronic communication between the nanobowl sites, and the CoP d-band center was downshifted with interfacial electron deficiency, which reduced excessive hydrogen adsorption and promoted the H₂ desorption process.

The FeP-CoP/Ti₃C₂T_x composite system demonstrated improved OER performance in alkaline media, with the MXene providing structural support and conductive channels while the bimetallic phosphide provided dense catalytic sites [13]. A particularly elegant approach used in 2024 involved NiCoP nanoneedle arrays grown directly on Ti₃C₂T_x MXene-coated Ni foam (NCP-MX/NF) via dip-coating hydrothermal synthesis followed by phosphorization. The resulting catalyst exhibited an HER overpotential of 72 mV at 10 mA cm⁻² and OER overpotential of 303 mV at 50 mA cm⁻², with a Tafel slope of 49.2 mV dec⁻¹ for HER, demonstrating well-optimized bifunctional performance [14].

3.3 MXene-Chalcogenide Heterostructures

MoS₂-Ti₃C₂T_x composites were extensively studied, with the critical insight that the orientation and phase of MoS₂ relative to the MXene substrate profoundly affect performance. Vertically aligned MoS₂ nanosheets grown on planar Ti₃C₂ via hydrothermal synthesis produce porous networks with expanded interlayer spacing of 9.4 Å, exposing previously inactive basal plane sites and achieving an HER overpotential of 95 mV and Tafel slope of 40 mV dec⁻¹ [15]. The 1T-MoS₂/Ti₃C₂ composite featuring a 3D interconnected network synthesized via magneto-hydrothermal methods demonstrated that the metallic 1T phase of MoS₂, stabilized by electron transfer from the MXene, dramatically outperforms its 2H counterpart in both conductivity and catalytic activity [16].

The CuS/Ti₃C₂Cl₂ system, utilizing an HF-free, environmentally benign Cl-terminated MXene, achieved an HER overpotential of 163 mV and a Tafel slope of 77 mV dec⁻¹ at 10 mA cm⁻², while demonstrating an OER overpotential of 334 mV at 50 mA cm⁻². The use of a fluoride-free MXene synthesis route represents an important advance toward greener catalyst fabrication, addressing concerns about HF toxicity in conventional MXene etching [13].

Table 1 summarizes benchmark electrochemical performances of selected MXene-based electrocatalysts reported between 2023 and 2025.

Catalyst System	HER η (mV@10 mA cm ⁻²)	OER η (mV@50 mA cm ⁻²)	Tafel HER (mV dec ⁻¹)	Medium	Ref.
Pt-NiCoP/Ti3C2Tx	26.5	—	—	1M KOH	[12]
NCP-MX/NF	72	303	49.2	1M KOH	[14]
MoS2/Ti3C2	95	—	40	0.5M H2SO4	[15]
CoP/Ti3C2Tx	135	—	48	0.5M H2SO4	[13]
CuS/Ti3C2Cl2	163	334	77	1M KOH	[17]
MoS2 QDs/Ti3C2Tx	220	—	72	0.5M H2SO4	[16]

Table 1. Electrochemical performance comparison of representative MXene-based electrocatalysts for HER and OER (2023–2025). η = overpotential; Tafel slope reflects rate-limiting step kinetics.

4. Single-Atom Catalysts (SACs) for Water Splitting

4.1 Principles and Advantages of SACs

Single-atom catalysts were the ultimate limit of catalyst miniaturization: single metal atoms, each perfectly coordinated by atoms from the support, with an atom economy of 100%. This configuration not only optimises atom economy but also removes the heterogeneity of surfaces of conventional nanoparticle catalysts, and provides a single type of active site for mechanistic and theoretical investigations. Since their definition by the Zhang group in 2011, SACs was evolved from novelty to a versatile design principle for a variety of reactions [17].

The benefits of using SACs for water splitting were threefold. First, the under-coordinated environment of single atoms greatly reduces the activation barriers for binding and activation of H₂O, H* and OOH* intermediates. Second, strong metal-support interactions (SMSI) provided by chemical bonding of single atoms to the support defect sites tune the d-band structure of the metal in ways impossible for bulk and nanoparticle catalysts. Third, the selectivity of SACs can be tuned by choosing the metal and local coordination environment (M-N₄, M-C₂N₂, M-S₄, etc.) to achieve desired catalytic properties [18]

4.2 SACs of Noble Metals - Reducing Precious Metal Usage

Rubidium single-atom systems were particularly popular in recent years. In 2023, Ru single atoms on amorphous MoO_{3-x} nanoflakes (Ru SAs-MoO_{3-x}) on nickel foam were prepared by hydrothermal-immersion-annealing. The amorphous oxide support provided a large number of oxygen vacancies as defect sites to bind Ru atoms and avoid sintering during operation. This catalyst showed excellent bifunctional HER and OER performance in alkaline media, and the corresponding electrolyzer showed excellent water and seawater splitting performance [19]. In 2025, a CoV-layered double hydroxide (LDH) with a Rubidium atom (CoVRu-LDH) was prepared via a one-step hydrothermal synthesis. Theoretical calculations showed that, compared to CoV-LDH, the d-band center of CoVRu-LDH was shifted up by

0.08 eV (from 0.15 to 0.23 eV), with high electron capture ability and stronger binding to reaction intermediates. In practice, the system delivered an OER overpotential of 263 mV required to reach 25 mA cm⁻² with a Tafel slope of 74.5 mV dec⁻¹ and 1.52 V to achieve 10 mA cm⁻² for overall water splitting [20].

4.3 Non-Precious Metal SACs - Earth Abundant Options

The Ni single-atom on oxygen-incorporated Mo₂C system (NiSA-O/Mo₂C) overcame a major roadblock in SACs: the poor activity of SACs on carbon supports for OER. Using a carbide (Mo₂C) with metal-like conductivity as the support and incorporating oxygen to modulate the surface chemistry, the authors developed a bifunctional SAC where the microenvironment of the Ni single atom is progressively adjusted by the reconstitution of Mo₂C. The new catalyst showed a performance that was much better than the bare Mo₂C support and traditional carbon-supported Ni-SACs for HER and OER [21]. Fullerene-supported SACs were a truly new frontier in 2025. The fullerene cages (C₆₀ and C₂₄) offer distinct electronic environments for metal atoms, and the electron affinity of fullerenes allows for strong metal-support interactions. New research shows that such C₆₀-based SACs with transition metals such as Pt, Ru and V are more active for HER/OER, are bifunctional and have spin-selective reaction pathways that are not possible with flat carbon supports. High-throughput methods, including machine learning, were used to screen metal-fullerene combinations, with the predictions validated by experiments [22].

4.4 Dual-Site and Bimetallic SACs

The idea of bimetallic synergistic SACs (two different isolated metal atoms in proximity that form cooperative sites) has emerged. This can allow the simultaneous optimization of different intermediates (H* for HER, OH* or OOH* for OER) at two different sites in the dual-site system. This method partially overcomes the scaling relationships constraining single-metal-element SACs. A Ni-Fe dual-site SAC on defective graphene, published in 2024, showed that the inter-site distance between Ni and Fe atoms could be tuned during the synthesis process, and that the optimal distances of 3.5-4.5 Å led to a synergy between the Ni-SAC and Fe-SAC that boosted both HER and OER beyond the sum of the individual Ni-SAC and Fe-SAC activities [23].

5. High-Entropy Materials for Water Splitting

5.1 The concept and design principle of high-entropy electrocatalysts

High-entropy alloys (HEAs), near-equi-molar multi-component solid solutions of five or more metallic elements, were originally reported in 2004 as structural materials. Their application as electrocatalysts was one of the most important developments in the field since 2020. The four defining characteristics of HEAs - the high-configurational-entropy stabilization of single-phase solid solutions, the severe lattice distortion arising from the different atomic sizes, the low diffusivity inhibiting elemental segregation, and the "cocktail effect" which leads to emergent properties from the multi-element composition - result in unique catalytic benefits: a high degree of surface heterogeneity that leads to a continuous distribution of active sites, and the strain-induced tunability of the binding energy of intermediate species that enables compositions to be tuned to occupy the peak of theoretical volcano plots [24]. By 2023-2025, high-entropy studies had broadened to include high-entropy oxides (HEOs), oxyhydroxides (HEOHs), sulfides, phosphides and carbonitrides, with each offering different electrochemical stability ranges and active-site environments. High-entropy oxyhydroxides (HEOHs) are especially promising OER catalysts, as the amorphous or semicrystalline hydroxide phases present metal cations in a mixture of coordination states [25].

5.2 High-Entropy Oxyhydroxides for OER

A landmark 2024 study from City University of Hong Kong reported a FeCoNiWCuOOH high-entropy oxyhydroxide material (FeCoNiWCuOOH@Cu) deposited on a three-dimensional double-continuous porous Cu support prepared by liquid metal dealloying. The five-element HEO material on the 3D Cu scaffold achieved OER overpotentials as low as 200 mV at 10 mA cm⁻² in 1.0 M KOH, with HER overpotential of only 18 mV, collectively enabling overall water splitting at a cell voltage of just 1.40 V at 10 mA cm⁻² [26]. This performance exceeds most non-noble metal benchmarks and places HEO materials firmly in the upper tier of bifunctional electrocatalysts.

The mechanistic origin of the exceptional OER activity in HEO materials was elucidated through a combination of in situ Raman spectroscopy, X-ray absorption spectroscopy (XAS), and DFT calculations. The multi-element cation environment creates local coordination geometries for Fe, Co, and Ni that simultaneously optimize different OER intermediate binding steps: Fe sites facilitate OH* adsorption, Co sites optimize O* formation, and Ni sites promote OOH* conversion. This site-specific task division — not achievable in single-element or binary systems — is the thermodynamic basis for the high performance [27].

5.3 High-Entropy Alloys — Strain Engineering and Composition Optimization

The strain effects of HEA electrocatalysts were studied. A PtIrCuNiCr HEA was demonstrated to be a bifunctional electrocatalyst with an overall water-splitting overpotential of about 190 mV at 10 mA cm⁻². Theoretical studies showed that the large lattice distortion of the HEA composition results in large strain on the surface, which leads to the d-band center shift for the Pt and Ir surface atoms and the change in the binding energies of the intermediates that drive the HER and OER activities towards the top of their respective volcano plots. DFT calculations revealed that strain effects can be systematically controlled by varying the configurational entropy of the alloys - higher entropy alloys with a greater diversity of atomic radii induce larger lattice distortion and stronger strain-activity relationships [28].

Lanthanide incorporation into HEA electrocatalysts was reported in ACS Nano in 2024, demonstrating that lanthanide elements such as La, Ce, or Pr, when confined in a high-entropy environment, undergo electron delocalization that amplifies their promoting effect on water splitting. The high-entropy lattice prevents lanthanide segregation (which would poison performance) while enabling their unique electronic properties to be expressed at the catalyst surface [29].

A self-circulating adsorption-desorption mechanism was described in ACS Sustainable Chemistry & Engineering for a non-noble HEA system. By designing a catalyst composition where different elements had complementary adsorption-desorption kinetics for H* and OH*, the system maintained a steady-state balance of active sites in different states of intermediate occupation, effectively preventing poisoning and maintaining high TOF throughout long-term operation [30].

Figure 2 below schematically depicts the multi-element active site diversity in high-entropy oxyhydroxide materials versus conventional single-element OER catalysts.

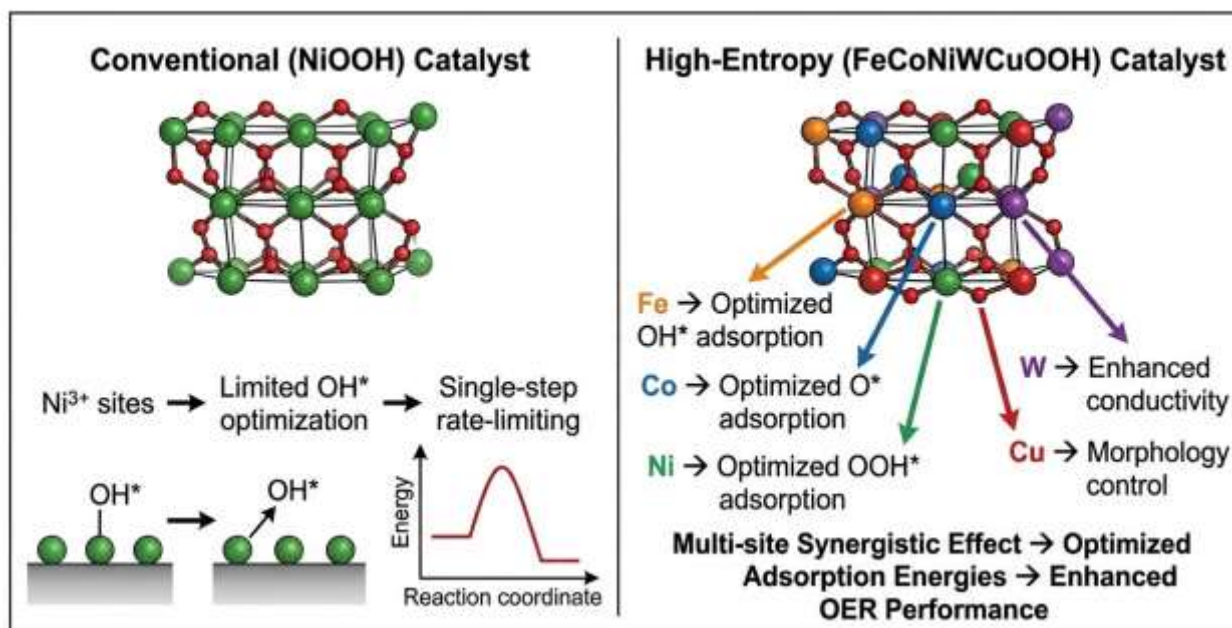


Figure 2. Schematic comparison of active site distribution in a conventional NiOOH OER catalyst versus a high-entropy oxyhydroxide (FeCoNiWCuOOH). The multi-element HEO provides task-specific sites for each OER intermediate step simultaneously, overcoming the single-element kinetic bottleneck.

6. Transition Metal Phosphides, Chalcogenides, and Carbides

6.1 Transition Metal Phosphides (TMPs)

Transition metal phosphides remained the most intensively studied non-precious HER and OER catalysts during the period 2023–2025, characterized by a decisive shift from monometallic phosphides toward complex heterostructure architectures that exploit interfacial synergy. The recognition that Ni₂P and CoP, while individually active, could be combined into Ni₂P/CoP heterojunctions with stable built-in electric fields (BIEFs) from the electronic redistribution at the interface has been transformative. A 2025 study demonstrated that the BIEF at Ni₂P/CoP heterojunctions accelerated both the Volmer step in HER and the OH* desorption step in OER, enabling industrial-current-density operation (>500 mA cm⁻²) [31].

The design principle of built-in electric fields was generalized beyond binary phosphide heterojunctions. Multiple interfaces coupling in double-sandwiched RGO/cobalt silicate/cobalt-iron phosphide architectures was shown in 2025 to generate layered BIEFs that sequentially accelerate charge transfer through the electrode structure, improving overall water-splitting performance significantly [32]. The WO₃/MoNi₄ heterostructure transition metal system (not a phosphide but analogous in its interface engineering logic) achieved an HER overpotential of 116.4 mV at 10 mA cm⁻² in 1M KOH, demonstrating the generality of BIEF-mediated enhancement [33].

Amorphous high-entropy oxysulfide phosphorus-doped catalysts reported in 2024 represent a convergence of the HEA and TMP design philosophies. The rational design of phosphorus-doped amorphous high-entropy oxysulfide for overall alkaline water splitting showed that amorphization — by disrupting long-range crystalline order — simultaneously maximizes active-site density, enhances electrolyte accessibility, and improves flexibility for electrode integration[34].

6.2 Transition Metal Chalcogenides — Phase Engineering Advances

Phase engineering of MoS₂, specifically the controlled synthesis and stabilization of the metallic 1T phase versus the semiconducting 2H phase, has matured significantly. The 1T phase offers three key advantages: metallic conductivity (10^4 to 10^5 S m⁻¹ versus 10^{-5} S m⁻¹ for 2H), increased hydrophilicity for better electrolyte contact, and a greater density of electrochemically active sites since the basal plane becomes catalytically active in the 1T phase. A phase-dependent growth strategy for Pt on MoS₂, published in Nature in September 2023 by City University of Hong Kong, demonstrated that Pt nanoparticles preferentially grow in registry with specific MoS₂ phases, and that precise control of the Pt-MoS₂ interfacial geometry produced dramatically enhanced HER activity compared to conventional Pt-on-MoS₂ systems [35].

Bimetallic chalcogenides, particularly NiCo, FeCo, and NiMo sulfide and selenide systems was shown to have outstanding bifunctional performance when integrated with conductive 2D supports. A 2025 study on MXene-supported 2D bimetallic chalcogenide electrocatalysts for electrochemical seawater splitting demonstrated that the bimetallic synergy, combined with the MXene conductivity and the increased layer spacing of the chalcogenide, collectively enabled both high activity and seawater corrosion resistance [16].

6.3 Layered Double Hydroxides (LDH) — Engineering Beyond Binary Systems

Ni(Co, Fe)-based LDH materials have served as the dominant OER catalyst family for alkaline water splitting, but the period 2023–2025 was a clear evolution from binary NiFe-LDH and CoFe-LDH toward ternary, quaternary, and vacancy-engineered systems. The introduction of a third metal (such as Mn, V, Cr, or Mo) into the LDH lattice systematically modulates the electronic environment of OER-active Ni and Fe sites. A 2024 study reported a dual-anion regulated CoFe-LDH/CoMoO₄ nanohybrid where tetraborate anions (B₄O₅(OH)₄²⁻) intercalated into CoFe-LDH interlayers and sulfate anions (SO₄²⁻) were incorporated into CoMoO₄, collectively achieving a simultaneous enhancement of both OER and HER activities (85 mV HER overpotential, 134 mV OER overpotential at 10 mA cm⁻² in 1M KOH) and remarkable long-term stability in seawater at an industrial current density of 1 A cm⁻² for 720 hours [36].

Table 2. Benchmark electrochemical performances of leading electrocatalyst materials across different categories (2023–2025). η = overpotential; all measurements in 1M KOH unless otherwise noted.

Material Class	Best η HER (mV)	Best η OER (mV)	Current Density (mA cm ⁻²)	Stability	Ref.
Ni ₂ P/CoP heterojunction	~80	~240	10–500	>100 h	[31]
Ru SAs-MoO ₃ -x	~55	~210	10	>40 h	[19]
CoV ₂ Ru-LDH SAC	—	263@25 mA	10–25	Stable	[20]
1T-MoS ₂ /Ti ₃ C ₂ MXene	95	—	10	>20 h	[15]
FeCoNiWCuOOH HEO	18	200	10	>50 h	[26]
Dual-anion CoFe-LDH	85	134	10	720 h @ 1A cm ⁻²	[36]
PtIrCuNiCr HEA	~30	~190	10	Stable	[28]

7. Direct Seawater Electrolysis — An Emerging Frontier

7.1 Challenges of Seawater as Electrolyte

The prospect of directly electrolyzing seawater using the virtually limitless resource of ocean water without energy-intensive desalination preprocessing has driven an entirely new subfield since approximately 2020. Seawater presents multiple challenges that do not exist in purified alkaline or acidic electrolytes: (1) the chloride ion (Cl^- , concentration $\sim 0.55\text{ M}$) undergoes oxidation via the chlorine evolution reaction (CER) at potentials within 480 mV of the OER potential in alkaline conditions, generating toxic Cl_2 , HClO , and ClO^- that corrode both catalyst and membrane; (2) magnesium and calcium ions precipitate as $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ on cathode surfaces during operation, blocking active sites and increasing resistance; (3) bacteria, organic matter, and sediment cause electrode fouling over time [37].

The thermodynamic proximity of OER ($E = 1.23\text{ V} + \eta$) and CER ($E = 1.72\text{ V}$ in neutral pH, dropping to $\sim 1.52\text{ V}$ in alkaline conditions) means that selectivity, not just activity, is the paramount design criterion for seawater anode materials. Operating in alkaline conditions provides a $\sim 480\text{ mV}$ thermodynamic window favoring OER over CER, but kinetic competition remains significant unless specific structural and compositional measures are taken [37].

7.2 Anion-Selective and Anti-Corrosion Strategies

The design of protective layers that selectively permit OH^- transport while blocking Cl^- diffusion was a breakthrough in 2024–2025. A CeO_x passivation layer was demonstrated to exhibit distinctive selective permeability, effectively inhibiting the diffusion of Cl^- and other redox-active ions while allowing OH^- and O_2 to pass freely [38]. This selectivity principle was generalized in a 'triple-defense' electrocatalyst for seawater oxidation, published in Nature Communications in 2025, where PO_4^{3-} enriched barriers and dispersed nanosized MnO_2 together formed a dual semipermeable blocking system that physically and electrochemically filtered Cl^- while maintaining OER activity [39].

Inhibiting surface reconstruction, the electrochemically driven phase transformation of catalysts under operating potentials, was identified as a key strategy for seawater corrosion resistance. A 2025 study demonstrated that by designing catalysts with a reconstruction-resistant composition, the material maintained 99.5% Faradaic efficiency for oxygen evolution in alkaline seawater, while an anion exchange membrane (AEM) electrolyzer based on this catalyst ($5 \times 5\text{ cm}^2$ active area) maintained a stable electrolysis current of 5000 mA for at least 250 hours, an order-of-magnitude improvement in durability over conventional anode materials under direct seawater conditions [40].

7.3 Dual-Anion Engineering for Seawater Stability

The dual-anion regulation strategy applied to the CoFe-LDH/CoMoO_4 system described in Section 6.3 was particularly significant for seawater applications. The tetraborate and sulfate anions built into the electrode preferentially occupy sites that would otherwise be chlorinated, providing built-in chemical protection without compromising the electrical accessibility of the active sites of Ni, Fe, and Co. The ability to operate at 1 A cm^{-2} for 720 hours in alkaline seawater was the longest reported stability at industrial current densities for a direct seawater anode catalyst in 2025 [38].

Redox-mediated decoupled seawater electrolysis (DSDE), introduced in 2024, takes a radically different approach. Rather than forcing the OER to compete with CER at the anode in a single-compartment cell, the DSDE system uses a ferricyanide/ferrocyanide ($[\text{Fe}(\text{CN})_6]^{3-/4-}$) redox mediator that undergoes oxidation at the anode instead of water. The O_2 is then produced in a separate reactor where the oxidized

mediator reacts with OH^- . This eliminates chlorine-containing byproducts and the corrosion they cause, at the cost of additional system complexity [41].

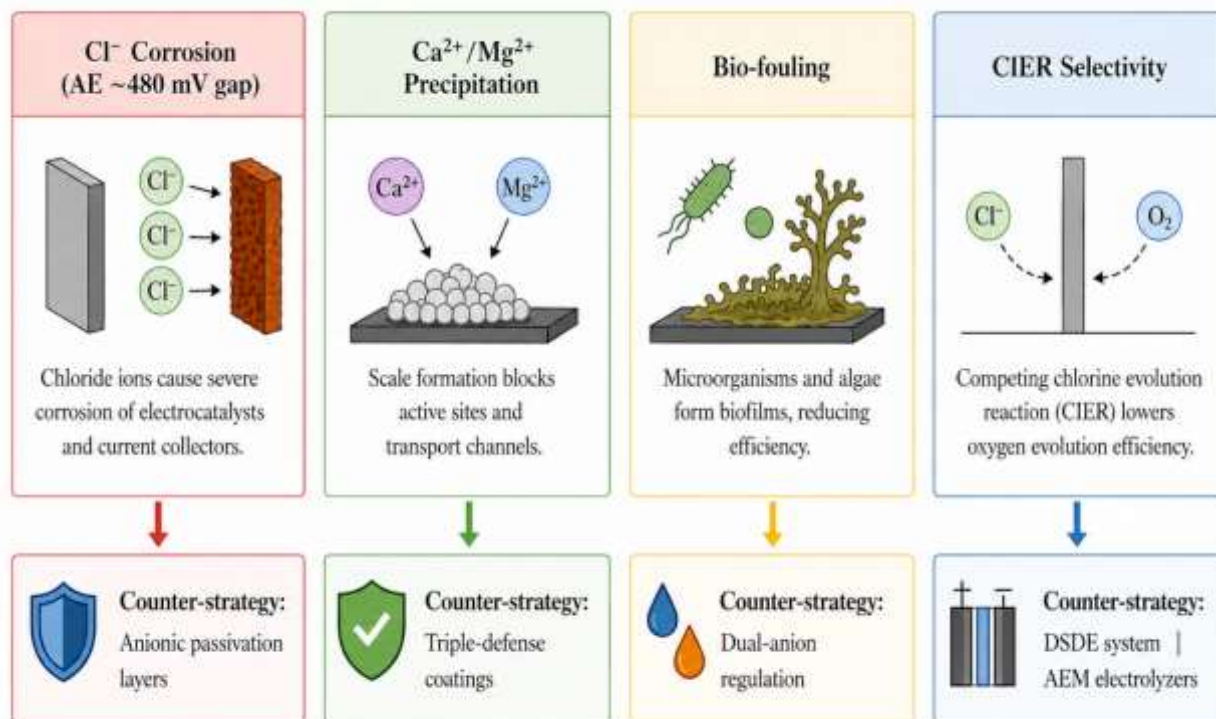


Figure 3. Challenge map for direct seawater electrolysis and the key materials strategies developed in 2023–2025 to address each challenge. The 480 mV thermodynamic window between OER and CIER in alkaline seawater is the central design constraint.

8. Emerging Directions and Crosscutting Advances

8.1 Machine Learning and Computational Screening

The sheer number of possible catalyst compositions - especially in the HEA and SAC spaces - has made computational screening a critical component of catalyst discovery. Machine learning interatomic potentials (MLIPs) derived from DFT calculations have been used to predict d-band centers, adsorption energies, and reaction barriers for thousands of compositions at only a fraction of the cost of DFT calculations, allowing systematic screening for promising compositions for synthesis. ML acceleration has been especially beneficial in the design of fullerene-supported SACs, in which crystal graph convolutional neural networks (CGCNNs) trained on SAC-support pairs have been able to predict HER performance to within DFT accuracy [22].

Active learning strategies, ML models were used to decide which experiments should be performed, and have also started to be applied to water splitting catalyst development, reducing the cycle of experimentation required to find the optimal composition from hundreds to tens. These methods can be further coupled with automated synthesis systems (robotic synthesis and high-throughput electrochemical screening) for closed-loop catalyst discovery [42].

8.2 Industrial-Scale Considerations — Membrane Electrode Assembly Integration

The gap between laboratory electrochemical performance (typically measured at 10 mA cm^{-2} on RDE or

GDE in half-cell geometry) and industrial electrolyzer performance (operated at 200–1000 mA cm⁻² in membrane electrode assemblies) was a persistent challenge. The period 2023–2025 was increased emphasis on demonstrating catalyst performance in relevant device geometries. Several of the catalysts reviewed here, including the dual-anion CoFe-LDH system and the reconstruction-free seawater anode, were tested in AEM electrolyzers at industrially relevant current densities and active areas, providing more reliable performance data for technology assessment [36,40].

The development of high-performance anion exchange membranes (AEMs) with improved OH⁻ conductivity, reduced Cl⁻ permeability, and chemical stability at alkaline pH was conducted with catalyst development. The combination of carefully designed seawater-resistant anode catalysts with next-generation AEMs that block Cl⁻ transport represents the most credible near-term pathway to practical seawater electrolysis at an industrial scale.

8.3 Self-Reconstruction as a Design Strategy

An initially counterintuitive but increasingly recognized phenomenon is that many of the best-performing OER catalysts are not the materials initially synthesized but rather the reconstructed phases formed in situ during electrochemical conditioning. Metal phosphides, chalcogenides, and alloys frequently undergo surface oxidation and hydroxylation under OER conditions, forming amorphous metal oxyhydroxide overlayers that are the actual catalytically active species. Design for positive reconstruction, where the precursor material is structurally transformed into a highly active oxyhydroxide while retaining its structure, was an explicit goal of catalyst design in the HEA and LDH areas. [25,36]

9. Current Challenges, Limitations, and Outlook

9.1 Key Unresolved Challenges

Despite the remarkable progress documented in this review, there are several problems that have not been solved and will be the focus of the next five years of research. The stability problem is probably the most important: although laboratory demonstrations at 10 mA cm⁻² typically report thousands of hours of stability, this drops to tens or hundreds of hours when operating at industrially relevant current densities (>200 mA cm⁻²) in real electrolytes (alkaline seawater or contaminated groundwater) for most non-precious catalysts. The causes of performance degradation - leaching of active elements, support corrosion, electrolyte contamination of active sites, rupture of the catalyst material under the pressure of gas evolution - are often poorly understood [46].

The OER scaling relation problem, the ~3.2 eV fixed difference between $\Delta G(\text{OOH}^*)$ and $\Delta G(\text{OH}^*)$ that sets a theoretical limit on the overpotential, has yet to be definitively overcome by any experimental system, as of 2025, despite many computational claims of how this might be achieved (e.g., via dramatic changes in reaction mechanism such as lattice-oxygen oxidation mechanisms, LOMs, or via unconventional catalyst structures, single-atom sites in small cavities)[43].

Identification of the active site was still elusive. Post-analysis of the catalyst structure after electrochemical tests were now complemented by in situ/operando probes (X-ray absorption spectroscopy, Raman, electron microscopy), but these techniques require access to synchrotron sources and complex setups and analyses. The community has not yet established consensus protocols for operando characterization, and discrepancies between different laboratories' measurements of ostensibly identical materials remain common

9.2 Roadmap to Practical Green Hydrogen Production

An assessment of the transition from present laboratory demonstration to commercially available green

hydrogen electrolyzers identifies four key milestones within the 2025–2030 time frame. In alkaline water electrolysis (AWE), the most mature technology, the principal material challenges remain: engineering OER catalysts that operate at 500 mA cm^{-2} and achieve $< 300 \text{ mV}$ overpotential for > 5000 hours in 30 wt% KOH solution (e.g., using non-precious elements). The HEO and the dual-anion LDH materials are currently the most reasonable candidates that have achieved these criteria.

In proton exchange membrane electrolysis (PEM), another high-efficiency technology, although operated under harsh acid/corrosive conditions, there are calls to substitute IrO_2 , as the OER catalyst, with a stable and earth-abundant catalyst. It is regarded as the most challenging open problem, and so far, none of the non-precious metal catalysts have shown adequate durability at acidic OER conditions. It is generally accepted that decreasing the content of precious metal (Ir) is most promising in the future through SACs or supported clusters.

For AEM electrolysis, which has the combination of efficiency of alkali water splitting and stack size of PEM electrolysis, the key challenges are to have high activity at acceptable current density and membrane compatibility; The AEM seawater electrolyzer demonstrations in 2025 show a great promise for this type of electrolysis, especially for distributed, coastal production where access to fresh water is not always possible.

10. Conclusions.

The current review highlights the most important advances in the materials for electrocatalytic water splitting reactions between 2023 and 2025. This period of swift development has clearly sped-up the adoption of technologies for generating green hydrogen, where the role of five families of materials has driven this advance, offering distinct benefits.

MXenes have been proven to be excellent bifunctional electrocatalytic supports, with $\text{NiCoP/Ti}_3\text{C}_2\text{Tx}$ showing similar HER overpotentials to Pt and a bifunctional cell potential of 1.40-1.60 V. It is worth mentioning that, in addition to being electron-conducting supports, MXenes have also been demonstrated to be electronic regulators by the shifting of the d-band centers of the supported catalysts via charge transfer.

SACs have allowed tailoring of the coordination between the metal sites and the support to achieve high atom efficiency and selectivity. These include fullerene supported SACs, bimetallic dual-site SACs and non-precious metal SACs in carbides.

High entropy materials have brought a new material concept: Complexity in composition was used to design multimetal single-site and optimize the interaction of multiple intermediates during OER; Furthermore, the strained surfaces of these alloys enable the materials to approach their maximum activity level, as per volcano-plots. FeCoNiWCuOOH is a typical example, which has an OER over-potential of 200mV and full water splitting potential of 1.40V.

Transition metal phosphides, chalcogenides and LDH materials supported on hierarchical structures with built-in electric fields or dual-anions demonstrated excellent stability exceeding the milestone 720 hours at 1 A cm^{-2} in alkaline seawater, which is a must for practical applications. The issues of directly using seawater were overcome through incorporation of anion-selective membranes or passivation layers, and dual-defence strategies, and the use of redox-mediated decoupled electrolysis, have opened new opportunities to avoid the Cl⁻ - corroding effect and ClER side reaction.

Integration of ML-based materials discovery, automated synthesis and operando characterization is accelerating the process of discovery and development. We anticipate that within the next five years, the

first generation of next-generation electrolyzers with non-precious metal catalysts based on these studies will be deployed on commercial scales, which will be the real breakthrough for green hydrogen.

References

1. N. America, Hydrogen Insights 2023 An update on the state of the global hydrogen economy , with a deep dive into North America, (2023).
2. Global Hydrogen Review 2025, (2025).
3. M.F. Lagadec, A. Grimaud, electrochemical systems, Nat. Mater. 19 (2020). <https://doi.org/10.1038/s41563-020-0788-3>.
4. J.A. Turner, Sustainable Hydrogen Production, 305 (2004) 972–975.
5. J. Zhu, L. Hu, P. Zhao, L. Yoon, S. Lee, K. Wong, Recent Advances in Electrocatalytic Hydrogen Evolution Using Nanoparticles, (2020). <https://doi.org/10.1021/acs.chemrev.9b00248>.
6. Y. Zheng, Y. Jiao, A. Vasileff, S. Qiao, The Hydrogen Evolution Reaction in Alkaline Solution : From Theory , Single Crystal Models , to Practical Electrocatalysts Angewandte, (2018) 7568–7579. <https://doi.org/10.1002/anie.201710556>.
7. A. Hickner, Trends in the Exchange Current for Hydrogen Evolution, (2005). <https://doi.org/10.1149/1.1856988>.
8. Y. Yan, Y. Xia, X. Wang, A review on noble-metal-free bifunctional heterogeneous catalysts for overall electrochemical water splitting, (2016) 17587–17603. <https://doi.org/10.1039/c6ta08075h>.
9. C. Ni, K. Wang, L. Jin, Y. Liu, J. Chen, L. Yang, C. Ji, Built-in electric field guides oxygen evolution electrocatalyst reconstruction, (2025) 658–668. <https://doi.org/10.1039/d4cc04740k>.
10. M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M.W. Barsoum, Two-Dimensional Nanocrystals Produced by Exfoliation of Ti_3AlC_2 , (2011) 4248–4253. <https://doi.org/10.1002/adma.201102306>.
11. M.R. Thalji, F. Mahmoudi, L.G. Bachas, MXene-Based Electrocatalysts for Water Splitting : Material Design , Surface Modulation , and Catalytic Performance, (2025) 1–43.
12. H. Niu, C. Huang, T. Sun, Z. Fang, X. Ke, R. Zhang, Electrocatalytic H_2 Evolution Hot Paper Enhancing Ni / Co Activity by Neighboring Pt Atoms in NiCoP / MXene Electrocatalyst for Alkaline Hydrogen Evolution, 202401819 (2024). <https://doi.org/10.1002/ange.202401819>.
13. I.H. Sajid, Recent advances in the role of MXene based hybrid architectures as electrocatalysts for water splitting, (2024) 6823–6847. <https://doi.org/10.1039/d3ra06725d>.
14. M. Jeong, S. Park, T. Kwon, M. Kwon, S. Yuk, S. Kim, C. Yeon, C. Lee, D. Lee, Interface Engineering via $\text{Ti}_3\text{C}_2\text{T}$, (2024). <https://doi.org/10.1021/acsami.4c00798>.
15. N.H. Attanayake, S.C. Abeyweera, D.R. Strongin, improved HER catalyst †, (2018) 16882–16889. <https://doi.org/10.1039/c8ta05033c>.
16. J. Joseph, J. Jeya, A.K. Ravindran, S.P. Muthu, R. Perumalsamy, MXene-supported 2D bimetallic chalcogenide electrocatalyst : Enhanced electrochemical seawater splitting, J. Power Sources 629 (2025) 235951. <https://doi.org/10.1016/j.jpowsour.2024.235951>.
17. B. Qiao, A. Wang, X. Yang, L.F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, Single-atom catalysis of CO oxidation using Pt_1/FeO_x , 3 (2011). <https://doi.org/10.1038/nchem.1095>.
18. N. Alam, T. Noor, N. Iqbal, Catalyzing Sustainable Water Splitting with Single Atom Catalysts : Recent Advances, 202300330 (2024). <https://doi.org/10.1002/tcr.202300330>.
19. D. Feng, P. Wang, R. Qin, W. Shi, L. Gong, J. Zhu, Q. Ma, Flower-Like Amorphous MoO_{3-x}

- Stabilized Ru Single Atoms for Efficient Overall Water / Seawater Splitting, 2300342 (2023) 1–10. <https://doi.org/10.1002/advs.202300342>.
20. Z. Yuan, Y. Yu, Q. Xie, L. Ding, W. Lei, H. Zhang, Y. Yao, Y. Wang, Enhanced Oxygen Evolution Kinetics via Single-Atom Catalyst Design: A Review, 2400916 (2025). <https://doi.org/10.1002/admi.202400916>.
21. M. Hou, L. Zheng, D. Zhao, X. Tan, W. Feng, J. Fu, T. Wei, M. Cao, J. Zhang, C. Chen, Microenvironment reconstitution of highly active Ni single atoms on oxygen- incorporated Mo₂C for water splitting, (2024). <https://doi.org/10.1038/s41467-024-45533-3>.
22. C. Li, S. Tong, D. Ma, H. Huang, X. Zheng, Y. Zhang, Fullerene-Supported Single-Atom Catalysts for Electrocatalytic Water Splitting: Progress, Challenges, and Machine Learning Perspectives, (2025) 1–21.
23. L. Wang, Z. Wei, Z. Sun, L. Zhu, Y. Gao, Z. Chen, S. Li, W. Chen, Carbon-based double-metal-site catalysts: advances in synthesis and energy applications, (2024) 11749–11770. <https://doi.org/10.1039/d4ta00727a>.
24. B.J. Yeh, S. Chen, S. Lin, J. Gan, T. Chin, T. Shun, C. Tsau, Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes **, (2004) 299–303. <https://doi.org/10.1002/adem.200300567>.
25. Y. Zhao, J. Wu, X. Cao, D. Li, P. Huang, H. Gao, Q. Gu, High-Entropy Materials for Water Splitting: An Atomic Nanoengineering Approach to Sustainable Hydrogen Production, 2506117 (2025). <https://doi.org/10.1002/adma.202506117>.
26. C. Zhang, D. Yin, Y. Zhang, Y. Sun, X. Zhao, W. Liao, J.C. Ho, A High-Entropy Oxyhydroxide with a Graded Metal Network Structure for Efficient and Robust Alkaline Overall Water Splitting, 2406008 (2024) 1–14. <https://doi.org/10.1002/advs.202406008>.
27. Y. Jiang, Z. Liang, J. Liu, H. Fu, C. Yan, Y. Du, Stimulating Electron Delocalization of Lanthanide Elements through High-Entropy Confinement to Promote Electrocatalytic Water Splitting, (2024). <https://doi.org/10.1021/acsnano.4c04176>.
28. B. Wang, iScience II Strain engineering of high-entropy alloy catalysts for electrocatalytic water splitting, ISCIENCE 26 (2023) 106326. <https://doi.org/10.1016/j.isci.2023.106326>.
29. J. Cai, H. Zhu, Surface-engineered nanostructured high- entropy alloys for advanced electrocatalysis, (2025).
30. Y. He, X. Zhu, C. Zhang, Z. Liu, B. Cao, L. Sheng, Y. Yang, Q. Feng, N. Wang, J.Z. Ou, Y. Xu, Self-Circulating Adsorption – Desorption Structure of Non-Noble High-Entropy Alloy Electrocatalyst Facilitates Efficient Water Splitting, (2023). <https://doi.org/10.1021/acssuschemeng.2c06888>.
31. T. Lin, H. Yang, J. Dong, C. Ni, X. Gao, J. Li, Constructing Ni₂P / CoP heterojunction with stable built-in electric field to boost overall water splitting at industrial current density, Fuel 396 (2025) 135282. <https://doi.org/10.1016/j.fuel.2025.135282>.
32. Y. Zhang, X. Tan, X. Pei, Y. Wang, S. Yi, Q. Wang, X. Zhu, C. Meng, C. Huang, INORGANIC CHEMISTRY Multiple interface coupling triggered built-in electric field over double-sandwiched RGO / cobalt silicate / cobalt-iron phosphide for improving the, (2025) 2439–2452. <https://doi.org/10.1039/d4qi02987a>.
33. X. Yin, X. Fu, X. Liu, Y. Wang, Y. Wang, Z. Liu, Construction of Transition Metal-Based MoNi₄ / WO₃ Heterostructure for Enhanced Hydrogen Evolution Reaction, (2025). <https://doi.org/10.1021/acs.iecr.4c04646>.

34. H. Zhang, J. Li, C. Dong, C. Zhu, J. Xu, L. Zuo, Rational design and dynamic reconstruction of phosphorus-doped amorphous high-entropy oxysulfide for efficient overall alkaline water splitting, *Chem. Eng. J.* 499 (2024) 156580. <https://doi.org/10.1016/j.cej.2024.156580>.
35. Z. Shi, X. Zhang, X. Lin, G. Liu, C. Ling, S. Xi, L. Li, Z. Li, X. Wang, G. Nam, J. Liu, Q. He, Phase-dependent growth of Pt on MoS₂ for highly efficient H₂ evolution, 621 (2023). <https://doi.org/10.1038/s41586-023-06339-3>.
36. T. Gao, W. Wang, Z. Zhang, W. Li, H. Gao, J. Liu, X. Zhao, Z. Liu, Y. Chen, Chemical Science EDGE ARTICLE Dual-anion regulation engineering enhances chloridion corrosion resistance for long-lasting, *Chem. Sci.* 16 (2025) 15684–15696. <https://doi.org/10.1039/D5SC03775A>.
37. Z.L. Wang, Triboelectric Nanogenerators as New Energy Technology for Self-Powered Chemical Sensors, (2013) 9533–9557.
38. P. Deng, R. Xue, J. Lu, P. Tsiakaras, Strategies for Designing Anti-Chlorine Corrosion Catalysts in Seawater Splitting, 2405749 (2025). <https://doi.org/10.1002/aenm.202405749>.
39. Z. Li, J. Liang, S. Hong, Y. Ren, M. Zhang, S. Sun, Z. Cai, C. Yang, H. Wang, Y. Luo, S. Liu, Y. Yao, F. Gong, X. Sun, B. Tang, A triple-defense electrocatalyst for robust seawater oxidation, (2025).
40. Y. Devi, R. Sundaresan, T.A. Zegeye, M.G. Tecson, G. Guo, W. Lin, Y. Shao, C. Tung, C. Chen, Surface Reconstruction-Free Stability Achieving Highly Anticorrosive Seawater Splitting, 16499 (2026) 1–12. <https://doi.org/10.1002/advs.202516499>.
41. T. Liu, C. Lan, M. Tang, M. Li, Y. Xu, H. Yang, Q. Deng, W. Jiang, Z. Zhao, Redox-mediated decoupled seawater direct splitting for H₂ production, *Nat. Commun.* (2024). <https://doi.org/10.1038/s41467-024-53335-w>.
42. W. Li, K. Liu, S. Feng, Y. Xiao, L. Zhang, J. Mao, Q. Liu, Journal of Colloid And Interface Science Well-defined Ni₃N nanoparticles armored in hollow carbon nanotube shell for high-efficiency bifunctional hydrogen electrocatalysis, *J. Colloid Interface Sci.* 655 (2024) 726–735. <https://doi.org/10.1016/j.jcis.2023.11.069>.
43. F.S. Vajedi, M.F. Carvalho, Exploring Recent Progress in First-Row Trimetallic Nanostructures and Their Derivatives for Electrocatalytic Water Splitting: A Comprehensive Review, (2025). <https://doi.org/10.1021/acsomega.5c05855>.