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Engineering Mn-doped Co-based heterostructures with oxygen vacancies toward efficient industrial-scale water oxidation catalysis

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- A $Mn_{0.10}Co_{0.90}\mbox{-}CoCo_2O_4/NF$ catalyst is designed by straightforward and efficient method.
- The catalyst exhibits attractive OER activity (223 mV@50 mA $\rm cm^{-2}$).
- The overall water splitting process exhibits a low cell voltage of 1.70 V at 100 mA cm $^{-2}$.
- The excellent properties result from the synergy of hierarchical design, oxygen vacancies, and Mn–Co interactions.

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Keywords: Heterostructure Oxygen vacancies Electronic structure Oxygen evolution reaction Surface reconstruction



ABSTRACT

Developing efficient and durable catalysts for the oxygen evolution reaction (OER) is essential for advancing water-splitting technologies. In this study, we present a self-supported $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF catalyst featuring a 2D/2D heterostructure, consisting of nanowire arrays coated with ultrathin nanosheets. This unique architecture forms interconnected 3D porous channels, enhancing electrolyte penetration, oxygen diffusion, and mass transport. X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and zeta potential (ζ) measurements reveal that Mn doping facilitates surface reconstruction and increases oxygen vacancies, optimizing the electronic structure and boosting catalytic activity. In situ Raman spectroscopy confirms that CoOOH is the active center, while operando electrochemical impedance spectroscopy demonstrates that strong electronic interactions at the heterogeneous interface enhance charge transfer. The $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF catalyst exhibits good electrocatalytic performance, achieving low overpotentials (178/233 mV at 10/50 mA cm⁻²) and exceptional stability (50 mA cm⁻² for 280 h) in alkaline electrolytes. This study underscores the synergistic effects of oxygen vacancy engineering, Mn–Co interactions, and a hierarchical structure in improving conductivity, active site accessibility, and reaction kinetics. $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF emerges as a promising, cost-effective alternative to noble metal catalysts for industrial-scale water electrolysis applications.

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1. Introduction

The increasing energy demands and pressing environmental challenges have intensified the pursuit of renewable energy capture and utilization technologies. The efficiency and power output of advanced energy storage and conversion systems are significantly influenced by electrochemical reactions involved in water splitting for hydrogen production [1–3]. Among these reactions, the oxygen evolution reaction (OER) is widely acknowledged as a critical bottleneck in the water-splitting process, playing a key role in generating clean hydrogen [4,5]. The sluggish kinetics of the four-electron transfer process impose substantial limitations on energy conversion efficiency. While high-performance catalysts such as RuO₂ and IrO₂ effectively reduce the overpotential, their widespread adoption is hindered by high costs and limited natural availability [6]. Recently, composite materials incorporating non-noble metals have gained significant attention for their high efficiency, excellent stability, and environmental compatibility [7,8].

The substitution of mixed-valence metals, such as Ni, Mn, Fe, or other secondary metals, enhances the activity and stability of OER catalysts. This enhancement is achieved by generating beneficial oxygen vacancies and modulating the electronic properties of active metal centers [9]. During the OER process, electron transfer occurs between adsorbed intermediates and the O 2p orbital rather than the Metal 3d orbital, shifting the redox center from the metal cation to the lattice oxygen. Recent research has highlighted the pivotal role of spontaneous oxidative surface reconstruction in metallic precatalysts, leading to the formation of high-valence metal oxides that act as the active phase during OER [10,11]. Moreover, oxygen vacancies serve as catalytic active sites, accelerating reaction kinetics. They facilitate reduced electron/mass transfer distances, optimize electron conductivity, and enable atomic doping to adjust coordination numbers and create unsaturated sites, significantly enhancing OER efficiency [12,13].

In addition to oxygen vacancies and surface reconstruction, previous studies have emphasized the importance of heterogeneous nanoarchitecture and surface/interface engineering in improving electrocatalytic performance [14-16]. These structural features boost electrocatalytic efficiency by increasing the density of exposed active sites, lowering intermediate adsorption energy, expanding interface contact areas, enhancing electrolyte penetration, and shortening charge transport distances [17–19]. For instance, Zhang et al. developed heterostructured NiFe₂O₄/FeNi₂S₄ nanosheets, demonstrating the effectiveness of interfacial engineering. These nanosheets enhance electrochemical activity through interfacial electronic coupling and rationally designed heterostructures derived from 2D nanostructures [20]. Furthermore, controlled oxygen vacancies have been shown to significantly improve OER activity in transition metal oxides by modulating bulk properties (e.g., energy levels, conductivity) and surface characteristics (e.g., molecular adsorption) [21].

Recent advancements in transition metal-based electrocatalysts, particularly those incorporating Mn and Co, underscore their potential as cost-effective and abundant alternatives with tunable electronic structures [22-24]. Mn-Co-based materials, including mixed oxides, spinels, and layered double hydroxides, demonstrate outstanding OER performance due to their synergistic effects, high conductivity, and stability in alkaline environments [25,26]. Incorporating Mn into Cobased frameworks modulates the electronic environment, optimizes the adsorption energies of oxygen intermediates, and enhances overall catalytic activity [27-29]. However, despite significant progress, challenges remain in improving activity, reducing synthesis costs, enhancing durability, and elucidating the underlying mechanisms of Mn-Co-based electrocatalysts. This study explores recent advancements, addresses key limitations, and optimizes the design of a highly efficient and sustainable OER catalyst with a specialized morphology and a straightforward synthesis approach.

Building on these considerations, we first synthesized the Mn-doped $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF heterostructure catalyst, which exhibits a

high concentration of oxygen vacancies. The synthesis was carried out via a simple hydrothermal method, followed by NaBH₄ reduction. The catalyst was in situ coupled with Mn-doped Co-based 2D/2D heterostructures, featuring nanowire arrays coated with ultrathin nanosheets, delivering exceptional OER performance. Comprehensive characterization techniques were employed to investigate the dynamic structural evolution and the relationship between self-reconstruction and catalytic activity. Mn doping effectively lowers the potential for highly active CoOOH generation, while the heterostructure significantly enhances the integration of nanowire arrays and ultrathin nanosheets. This architecture accelerates reaction kinetics and improves mass transfer, boosting OER performance. The synthesized monolithic structure is an efficient OER electrode, achieving an overpotential of 233 mV at 50 mA cm⁻² and substantial catalytic activity and electrochemical stability. In watersplitting tests, the $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF ⁽⁺⁾||Pt/C⁽⁻⁾ electrocatalyst outperforms the $RuO_2^{(+)}||Pt/C^{(-)}$ benchmark, ranking among the highest-performing transition metal compound-based catalysts.

2. Experimental sections

2.1. Materials

Manganese (II) acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O, 99 %, Aladdin), cobaltous (II) nitrate hexahydrate (Co(CH₃COO)₂·6H₂O, 99.5 %, Aladdin), urea (CO(NH₂)₂, 99.0 %, Aladdin), ammonium fluoride (NH₄F, 96.0 %, Aladdin), sodium borohydride (NaBH₄, \geq 98.0 %, Xilong), potassium hydroxide (KOH, 90 %, Macklin), ethanol (C₂H₅OH, 99.7 %, Xilong), Nafion (5 wt%, Alfa Aesar), Pt/C (20 wt% Pt, Sinero), nickel foam (NF) used as a substrate was obtained from Suzhou Sinero Technology Co, Ltd (with a thickness of 1.6 mm). RuO₂ powder was prepared by directly annealing RuCl₃·3H₂O (37 %, Inno-chem) at 400 °C in air. All reagents were commercially available and could be used directly without further purification.

2.2. Synthesis of MnO(OH)-CoCo₂O₄/NF

A 1.5 cm \times 3.5 cm piece of nickel foam (NF) was ultrasonically cleaned sequentially in 0.5 M H₂SO₄, ethanol, and deionized water for 15 min each to ensure the removal of surface impurities. Subsequently, 1.0 mmol Co(CH₃COO)₂·6H₂O, 2.0 mmol Mn(CH₃COO)₂·4H₂O, 4.0 mmol NH₄F, and 4.5 mmol CO(NH₂)₂ were dissolved in 50 mL deionized water to form a uniform solution under magnetic stirring at room temperature. The treated NF was immersed in the solution and transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 140 °C for 7 h and then cooled naturally to room temperature. The resulting product, MnO(OH)-CoCo₂O₄/NF, was washed several times with ethanol and deionized water and then dried at 60 °C for 3 h.

2.3. Synthesis of Mn(OH)2-CoCo2O4/NF

The pre-prepared MnO(OH)-CoCo₂O₄/NF was placed in the tube furnace and gradually heated to 400 °C at a rate of 5 °C min⁻¹ for 120 min under a nitrogen atmosphere to obtain Mn(OH)₂-CoCo₂O₄/NF.

2.4. Synthesis of Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF

0.1 g NaBH₄ was dispersed in 20 mL of deionized water under ultrasonic treatment. The Mn(OH)₂-CoCo₂O₄/NF was subsequently introduced into the solution and reacted at room temperature for 5 h. The electrode was rinsed with deionized water and ethanol and then vacuum-dried. Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF nanosheet arrays were successful. A series of samples with varying Co/Mn ratios (2.5/0.5, 1.5/1.5, 0.5/2.5, 3/0, and 0/3) and different hydrothermal synthesis temperatures (180 °C, 160 °C, 120 °C, and 100 °C) were synthesized using the same method.

For comparison, Mn₃O₄-Co(OH)₂/NF was directly reduced from

 $MnO(OH)-CoCo_2O_4/NF$ using NaBH₄ solution without undergoing heat treatment at 400 °C. Co(OH)_2-CoCo_2O_4/NF and Mn_2O_3-Mn(OH)_2/NF were synthesized like Mn_{0.10}Co_{0.90}-CoCo_2O_4/NF.

2.5. Synthesis of RuO₂/NF and 20 wt% Pt/C/NF electrodes

RuO₂ (2 mg) and 20 wt% Pt/C were dispersed in a solution containing 200 μ L deionized water, 200 μ L ethanol and 10 μ L Nafion (5 wt %) solution. The mixture was sonicated for 30 min to achieve a homogeneous solution. This solution was then drop-cast onto a clean NF (1 cm \times 1 cm) and allowed to dry in air.

3. Results and discussion

3.1. Synthesis and characterizations

The catalyst's epitaxial growth mode reduces the interfacial energy of the hybrid nanostructures and facilitates the formation of highly crystalline alloy laminates [30,31]. Consequently, transition metal

alloys with open structures and highly crystalline ultrathin morphologies, grown epitaxially on substrates, exhibit superior catalytic performance and stability. The preparation process for the Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF catalyst is illustrated in Fig. 1a. Initially, the MnO(OH)-CoCo₂O₄/NF precursor was hydrothermally grown on a pretreated NF substrate and subsequently annealed to form Mn(OH)2-CoCo2O4/NF nanowire arrays, as depicted in Fig. 1b and c. The catalyst morphology transitioned from nanowires to a more slender structure during the synthesis. Finally, the Mn(OH)2-CoCo2O4/NF was subjected to a NaBH4 solution via an impregnation reduction method, yielding the Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF catalyst. A second solvothermal reaction further decorated the nanowire structure with uniform nanosheets (Fig. 1d). SEM images reveal that the nanowire arrays are coated with ultrathin, undulating nanosheets, creating an intersecting 2D/2D heterostructure with interconnected 3D porous channels. This configuration enhances electrolyte penetration and oxygen diffusion. In contrast, alternative structures exhibit notable differences: Mn₃O₄-Co(OH)₂/NF consists of nanorods (Fig. S2a), Mn₂O₃-Mn(OH)₂/NF features distinct blocky particles densely anchored on NF (Fig. S2b), and Co(OH)2-



Fig. 1. (a) Schematic illustration of the preparation of $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF. SEM images of (b) MnO(OH)-CoCo₂O₄/NF, (c) $Mn(OH)_2$ -CoCo₂O₄/NF, and (d) $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF. (e) TEM image, (f) High-resolution (HR)-TEM image, (g) as well as the intensity profile of corresponding areas, (h) AFM image, (i) HAADF-STEM image, and (j-l) elemental mappings (O, Co, and Mn) of the $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF.

CoCo₂O₄/NF presents a nanocotton-like morphology (Fig. S2c). Microsheet structures of CoMn-X-Y/NF synthesized using varying Co/Mn ratios (2.5/0.5, 1.5/1.5, and 0.5/2.5) show subtle differences (Fig. S3a-c). Interestingly, hydrothermal temperature variations (100 °C, 120 °C, 160 °C, and 180 °C) have minimal impact on the synthesis morphology of CoMn/NF-X (Fig. S4a-d). A transmission electron microscopy (TEM) image (Fig. 1e) confirms the Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF catalyst's nanowire structure, with the outer nanosheet removed. High-resolution TEM (HR-TEM) images (Fig. S5) further identify the Mn_{0.10}Co_{0.90} and CoCo₂O₄ phases on the surface. As shown in Fig. 1f and g, the lattice spacings of 0.128 nm and 0.257 nm correspond to the (011) and (620) crystal planes of spinel Mn_{0.10}Co_{0.90} and CoCo₂O₄, respectively. Atomic force microscopy (AFM) measurements (Fig. 1h) indicate that the outer layers of Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF have an average thickness of 3.7 nm. This ultra-thin layer increases the exposure of reactive sites, thereby boosting the nanocatalyst's inherent electrocatalytic activity. Energydispersive X-ray spectroscopy (EDS) mapping (Fig. 1i-l) confirms the uniform distribution of O. Co. and Mn elements across the catalyst.

The crystal structure of the catalyst was analyzed using X-ray diffraction (XRD). As shown in Fig. S6a, the initial hydrothermal reaction produced MnO(OH)-CoCo₂O₄/NF. After high-temperature calcination, this material transformed into Mn(OH)₂-CoCo₂O₄/NF, as depicted in Fig. S6b. Using NaBH₄ as a reducing agent, Mn(OH)₂-CoCo₂O₄/NF was further reduced to Mn_{0.10}Co_{0.90} (JCPDS: 78-1991) and CoCo₂O₄ (JCPDS: 80-1544), as illustrated in Fig. 2a. Notably, MnO(OH)-CoCo2O4/NF can also be converted to Mn3O4-Co(OH)2/NF via reduction in an aqueous solution without requiring high-temperature heat treatment (Fig. S6c). For comparison, precursor compounds loaded with only Co or Mn on NF underwent reduction in an aqueous solution, forming Co (OH)₂-CoCo₂O₄/NF and Mn₂O₃-Mn(OH)₂/NF, respectively (Fig. S7a-b). Raman spectroscopy was used to analyze the bonding information of the catalysts. The Raman spectrum of $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF (Fig. 2b) shows significant peaks at 177, 312, and 362 cm⁻¹, corresponding to Co-O, while a peak at \sim 587 cm⁻¹ is attributed to the Co_xMn_vO index, confirming the presence of both Mn and Co [32-34]. Additional peaks at \sim 191 and 486 cm⁻¹ are assigned to Mn-O bending vibrations, and the peak at \sim 660 cm⁻¹ corresponds to Mn-O stretching vibrations. The MnO stretching peak was used to evaluate the bond force constant (*k*) using Hooke's law: $\omega = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu^2}}$ where ω is the Raman shift (cm⁻¹) of the Mn-O stretching vibration, *c* is the speed of light, and μ is the effective mass of the Mn-O bond [24]. A red shift in the Mn-O peak (from 687 cm⁻¹ to 620 cm⁻¹) and decreased intensity after Co substitution indicate a weakened Mn-O bond in Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF compared to Mn₂O₃-Mn(OH)₂. This bond weakening enhances the redox properties [35,36].

The type and concentration of defects in the catalyst were further evaluated using electron paramagnetic resonance (EPR) spectroscopy. No significant variation was observed in the EPR spectra of MnO(OH)-CoCo₂O₄/NF and Mn(OH)₂-CoCo₂O₄/NF. However, Mn_{0.10}Co_{0.90}- $CoCo_2O_4/NF$ exhibited a symmetric EPR signal around g = 2.005, associated with unpaired electrons of oxygen vacancies (Fig. 2c). Oxygen vacancy formation in Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF occurs due to the reduction of oxygen atoms to O2 or H2O via electron donation from NaBH₄, resulting in the escape of these species and the creation of vacancies [37]. The signal intensity in the EPR spectrum indicates the concentration of oxygen vacancies, with higher intensity corresponding to more defects. Interestingly, the catalyst synthesized at 140°C exhibited the highest signal intensity (Fig. S9), indicating a higher concentration of oxygen vacancies and a more defective structure [38]. These vacancies enhance oxygen mobility and storage capacity, further improving catalytic activity [27]. EPR spectra of Mn₃O₄-Co(OH)₂/NF (g = 2.17), Co(OH)₂-CoCo₂O₄/NF (g = 2.17), and Mn₂O₃-Mn(OH)₂/NF (g = 2.12) indicate the presence of metallic vacancies (Fig. S8) [39]. Brunauer-Emmett-Teller (BET) analysis of Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF, Co(OH)₂-CoCo₂O₄/NF, and Mn₂O₃-Mn(OH)₂/NF (Figs. 2d and S10) revealed type III isotherms with mesoporous characteristics and distinct hysteresis loops. $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF exhibited the highest BET surface area (76.20 m² g⁻¹), compared to Co(OH)₂-CoCo₂O₄/NF (54.40 $m^2~g^{-1})$ and $Mn_2O_3\text{-}Mn(OH)_2/\text{NF}$ (41.53 $m^2~g^{-1}).$ The higher surface area of Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF enhances the exposure of active sites, facilitates electrolyte diffusion, and improves gas emission properties, thereby contributing to its superior catalytic performance [40,41].

X-ray photoelectron spectroscopy (XPS) analysis was performed to



Fig. 2. (a) XRD pattern of $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF. (b) Raman spectra, and (c) electron paramagnetic resonance (EPR) spectra of the different catalysts. (d) Nitrogen adsorption–desorption isotherms and corresponding pore size distribution of $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF.

investigate the catalysts' surface chemical composition and valence states. The survey spectra (Fig. S11a) confirm the presence of O, Co, and Mn elements in Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF. The high-resolution C 1 s spectrum (Fig. S11b) was used as a reference for correcting the binding energies of other elements. The Co 2p XPS spectra of Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF and Co(OH)₂-CoCo₂O₄/NF (Fig. 3a) were deconvoluted into three characteristic peaks. In the Co $2p_{3/2}$ XPS spectrum of Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF, sub-peaks at 779.9, 781.9, and 785.5 eV correspond to Co^{3+} , Co^{2+} , and a satellite peak, respectively [42]. The absence of Co⁰ in the spectrum is attributed to the predominance of cobalt oxides, which obscure the signals from smaller alloy components [43]. A 0.30 eV negative shift in the Co 2p peak for Mn_{0.10}Co_{0.90}-CoCo2O4/NF, compared to Co(OH)2-CoCo2O4/NF, indicates electron transfer at the heterointerfaces, modulating the electronic structure through strong interfacial interactions [44]. The high-resolution Mn 2p XPS spectrum of $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF (Fig. 3b) reveals a Mn $2p_{3/2}$ peak at 637.6 eV, attributed to metallic Mn⁰ within the CoMn alloy, consistent with XRD and TEM data. Additional peaks at 640.8, 642.8, and 646.1 eV correspond to Mn^{2+} , Mn^{3+} , and Mn^{4+} , respectively [38]. Furthermore, a 0.20 eV positive shift in Mn 2p peaks for Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF indicates electron transfer between Mn and Co. The presence of highly negative charges in the catalyst optimizes binding energy, facilitating the OER process [45,46]. The deconvolution of the O 1 s XPS spectra (Fig. 3c) reveals three peaks at 529.7, 531.2, and 532.2 eV, corresponding to lattice oxygen peak (OL) [47], oxygen vacancy peak (O_v) [48], and chemisorbed oxygen peak (O_{ads}) [24], respectively. Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF exhibits a higher concentration of oxygen vacancies (44.10%), surpassing that of Co(OH)₂-CoCo₂O₄/NF (38.70%) and Mn₂O₃-Mn(OH)₂/NF (24.83 %), consistent with the EPR results. These increased oxygen vacancies enhance the electronic structure,

improve conductivity, and facilitate the adsorption of OER intermediates, thus boosting reaction kinetics and oxygen evolution efficiency [13,49].

Ultraviolet photoelectron spectroscopy (UPS) was utilized to examine the electronic properties of Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF and its enhanced intrinsic activity. The work functions (WF) of Mn_{0.10}Co_{0.90}-CoCo2O4/NF, Mn(OH)2-CoCo2O4/NF, and MnO(OH)-CoCo2O4/NF were measured as 5.89, 6.20, and 6.45 eV, respectively (Fig. 3d-e). The lower WF of Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF indicates facilitated electron transfer from the catalyst's interior to its surface, enabling charge redistribution [50]. This observation aligns with the XPS analysis, confirming enhanced electron exchange with reactants and accelerated reaction kinetics [51]. Moreover, the valence band maximum (E_v) of $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF is 0.72 eV, the lowest among the samples. This proximity of the valence band to the Fermi level (Ef) enhances conductivity, accelerates electron transfer, and improves reaction kinetics [52]. Zeta potential (ζ) measurements were conducted to assess the surface charge properties of the catalysts under alkaline conditions. As shown in Fig. 3f, Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF exhibits the highest surface electronegativity (-15.43 mV), compared to Co(OH)₂-CoCo₂O₄/ NF (-3.39 mV) and Mn₂O₃-Mn(OH)₂/NF (-0.86 mV). This increased electronegativity, attributed to more significant OH⁻ adsorption, facilitates rapid charge accumulation and enhances OER efficiency in alkaline media [53–55].

3.2. Electrocatalytic performance

The efficiency of the designed catalysts for the OER was systematically evaluated in a 1.0 M KOH solution using a standard three-electrode arrangement. All potentials were adjusted for 100 % *iR* compensation



Fig. 3. High resolution XPS spectra of (a) Co 2p, (b) Mn 2p, and (c) O 1 s of designed catalysts. (d) UPS spectra and (e) band structure alignment of designed catalysts. (g) Zeta potentials of designed catalysts.

and calibrated against the reversible hydrogen electrode (RHE, Fig. S1). Considering the feasibility of the synthesis method, the main sample Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF was synthesized in three batches, and its performance was evaluated to determine the optimal values. To ensure result reliability, statistical analysis and error bar assessments were conducted on the synthesized data (Figs. S12-13) [56]. Fig. 4a and b display the linear sweep voltammetry (LSV) curves and the corresponding Tafel slopes, respectively. The Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF catalyst demonstrated overpotentials of 178 mV and 233 mV to achieve current densities of 10 and 50 mA $\rm cm^{-2}$, respectively, along with an ultra-low Tafel slope of 70.49 mV dec⁻¹, outperforming all other tested electrocatalysts (Fig. 4c). These results indicate that Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF exhibits faster reaction kinetics than the other catalysts [57]. The electrochemically active surface area (ECSA) (Fig. 4e) was estimated from the electrochemical double-layer capacitance (C_{dl}) (Fig. 4d), derived from cyclic voltammetry (CV) curves in the non-Faradaic region (Fig. S14a-g). Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF showed significantly higher C_{dl} (499.1 mF cm⁻²) and ECSA (10,398.0 cm²) than the other catalysts. This structural advantage increases the number of accessible active sites, thereby enhancing the catalytic activity of $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF during oxygen catalysis [58]. A comparison of Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF with other recently developed nonprecious metal catalysts (Fig. 4f and Table S1) highlights its superior OER overpotential and Tafel slope. Furthermore, the turnover frequency (TOF) analysis (Fig. 4g) reveals that Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF exhibits significantly higher intrinsic OER activity than the other catalysts, confirming its exceptional electrocatalytic performance [59]. Nyquist plots (Fig. 4h) indicate minimal charge transfer resistance for Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF compared to other catalysts, further demonstrating its enhanced ability to facilitate charge transfer and reaction kinetics for OER [60]. The Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF catalyst exhibited outstanding catalytic performance under optimized conditions achieved by adjusting the solution temperature to 140 °C and the Co/Mn molar ratio to 2:1 (Figs. S15-18). These optimizations produced a synergistic effect that maximized performance by fine-tuning the hydrothermal reaction temperature and the Co/Mn ratio. The surface vacancies in electrocatalysts can have a positive impact on electrochemical reactions. We then investigated the effect of oxygen vacancy concentration on OER performance. The LSV curves in Fig. 4a and Fig. S17a demonstrate that the catalyst Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF, synthesized at 140 °C, exhibits



Fig. 4. (a) LSV polarization curves, (b) Tafel slopes, and (c) summary of overpotentials (at 10 and 50 mA cm⁻²) and Tafel slopes of comparable catalysts in 1.0 M KOH. (d) C_{dl} and (e) summary of ECSA of designed catalysts. (f) Comparison of overpotential (at 10 mA cm⁻²) and Tafel slopes for various state-of-the-art OER catalysts. (g) Turnover frequency values and electrochemical impedance spectroscopy (EIS) data of the prepared catalysts are presented. (h) Chronopotentiometry of $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF at 50 mA cm⁻² (the inset displays the contact angle test for designed catalysts).

the best OER catalytic activity. The presence of abundant oxygen vacancies and associated unpaired electrons in $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF not only modifies the local electronic structure and orbital coupling but also exposes additional active sites, enhancing the adsorption of reactive intermediates and improving the catalyst's catalytic performance. Considering the potential impact of synthesis parameters on material quality, we performed a statistical analysis of the synthesized catalysts but found no discernible patterns (Table, S2). This suggests that the final material quality may be influenced by variations in morphology and loading amount on the carrier.

Moreover, the OER performance of $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF was evaluated under acidic (0.5 M H₂O₄) and neutral (0.1 M phosphatebuffered saline, PBS) conditions. As shown in Fig. S19, $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF exhibited poor OER activity in both 0.5 M H₂O₄ and 0.1 M PBS.

Stability is a critical parameter for industrial applications, and $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF demonstrated exceptional durability in a basic solution, maintaining stable performance for over 280 h at 50 mA cm⁻². The hydrophilicity of the catalyst surface was evaluated using static water contact angle measurements (Fig. 4i). The $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF electrode exhibited superhydrophilic properties, with water droplets permeating the electrode surface instantly, resulting in static contact angle of zero. The contact angles for Co(OH)₂-CoCo₂O₄/NF and Mn_2O_3 -Mn(OH)₂/NF were 40.2° and 131.2°, respectively. The superior wettability of $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF is attributed to the increased surface area and roughness created by its interconnected heterogeneous interface. This enhanced hydrophilicity improves electrolyte–electrode contact and diffusion, facilitating mass and charge transfer and accelerating reaction kinetics [61,62].

Pt/C cathode to test overall water splitting capabilities (Fig. 5a). The polarization curves (Fig. 5b) show that the Mn_{0.10}Co_{0.90}-CoCo₂O₄/ $NF^{(+)}||Pt/C^{(-)}$ electrolyzer outperforms the commercial $RuO_2^{(+)}||Pt/C^{(-)}|$ electrolyzer, particularly at higher current densities. As illustrated in Fig. 5c, the $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF⁽⁺⁾||Pt/C⁽⁻⁾ electrolyzer requires only 1.70, 1.75, 1.82, and 1.89 V to reach current densities of 100, 200, 500, and 1000 mA cm^{-2} , respectively. By contrast, the commercial $RuO_2^{(+)}||Pt/C^{(-)}$ electrolyzer demands higher cell voltages to achieve equivalent current densities. Fig. 5d and Table S3 demonstrate that the $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF⁽⁺⁾||Pt/C⁽⁻⁾ electrocatalyst surpasses the performance of most previously reported noble metal-free catalysts for overall water splitting in alkaline media, particularly at a current density of 10 mA cm⁻². Stability tests (Fig. 5e) reveal that the $Mn_{0.10}Co_{0.90}$ - $CoCo_2O_4/NF^{(+)}||Pt/C^{(-)} electrolyzer\ maintains\ exceptional\ stability,$ operating continuously at a current density of 100 mA cm⁻² for over 135 h. These results highlight the catalyst's efficiency and robustness, making it a strong candidate for practical water electrolysis applications. Moreover, Fig. 5f illustrates the feasibility of powering the $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF⁽⁺⁾||Pt/C⁽⁻⁾ electrolyzer using a solar cell. The production, accumulation, and release of hydrogen and oxygen bubbles on the electrode surface confirm the electrolyzer's ability to achieve overall water splitting under solar input. These findings underscore the potential of the Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF anode for large-scale industrial applications in renewable energy technologies. Due to the current limitations of our experimental setup, large-scale industrial applications are not yet feasible. However, we recognize the importance of this aspect and will consider it a key direction for future research.

3.4. Dynamic transformation analysis

3.3. Overall water splitting performance

To further evaluate the OER performance of $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/ NF in an industrial alkaline electrolyzer, it was paired with a commercial

Following the OER stability test of $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF, SEM and TEM were utilized to examine the morphology and surface chemical states. SEM images confirmed the retention of the catalyst's nanowire structure (Fig. 6a). Furthermore, HR-TEM analysis revealed a lattice



Fig. 5. (a) Illustration of the overall water splitting in a two-electrode system. (b) LSV curves of overall water splitting for $Mn_{0.10}Co_{0.90}$ - $CoCo_2O_4/NF^{(+)}||Pt/C^{(-)}$ and $RuO_2^{(+)}||Pt/C^{(-)}$ in 1.0 M KOH. (c) Comparison of the required voltages at different current densities. (d) Comparison of the cell voltage for $Mn_{0.10}Co_{0.90}$ - $CoCo_2O_4/NF$ at 10 mA cm⁻² with recently reported catalysts. (e) Chronopotentiometry test at 100 mA cm⁻². (f) Actual operation diagram of water splitting powered by sunlight.

spacing of 0.219 nm corresponding to the (006) plane of CoOOH, indicating structural stability after the OER stability test (Fig. 6b). CV measurements illustrated changes in the valence states of active species during the OER process. The catalysts were preconditioned for 10 cycles at a scan rate of 50 mV/s, with the resulting steady-state CV curve shown in Fig. 6c [63]. Upon applying potential, electrons migrated to the collecting electrode (NF). At the same time, holes oxidized Co^{2+} to Co^{3+} [64]. For Co(OH)₂-CoCo₂O₄/NF, the Co^{2+}/Co^{3+} redox transition was observed at approximately 1.42 V. In contrast, for $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF, it occurred at around 1.40 V. This shift suggests that Mn substitution facilitates cobalt oxidation at a lower potential, aiding surface reconstruction [65].

In-situ Raman spectroscopy was employed to investigate the catalysts' dynamic structural evolution during OER and identify the characteristics of reconstructed active species [66]. Peaks observed at 490 and 610 cm⁻¹, corresponding to the phonon modes of Co_3O_4 , emerged at the open circuit potential (OCP), signifying the formation of Co spinel oxides on the surface (Fig. 6d) [67]. When the applied potential increased to 1.4 V, these peaks disappeared, indicating complete phase conversion. Beyond 1.4 V, new peaks at 447 and 554 cm⁻¹, corresponding to the E_g and A_{1g} lattice modes of CoOOH, respectively, became prominent, highlighting their role as active centers during the

OER [65]. The low-frequency region of the EIS Bode plots revealed nonuniform charge distribution associated with the oxidation of the electrode interior on the catalyst surface during OER [55]. Figs. 6e, f, and S20 show a rapid decrease in charge transfer resistance (R_{ct}) for Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF, with peaks related to oxygen OER at 1.35 V. This observation indicates rapid oxygen species adsorption at lower potentials, leading to the accumulation of oxygen-containing intermediates on active Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF sites. It also confirms that Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF facilitates faster charge accumulation, enhancing OER performance in alkaline media [53,68]. To further explore the surface structure of $Mn_{0.10}Co_{0.90}\mbox{-}CoCo_2O_4/NF$ under OER conditions, XPS analysis was conducted after durability testing (Fig. 6g-h). The ratios of Co^{3+}/Co^{2+} , Mn^{2+}/Mn^0 , Mn^{3+}/Mn^{2+} , and Mn^{4+}/Mn^{2+} were calculated from the XPS spectra of $Mn_{0.10}Co_{0.90-}$ CoCo₂O₄/NF before and after the OER stability test (Fig. 6i). Post-OER. the Co^{3+}/Co^{2+} ratio increased from 1.32 to 1.61, reflecting greater exposure of Co³⁺ species, which enhance catalytic activity during OER [69]. Conversely, the Mn^{2+}/Mn^{0} ratio decreased from 6.03 to 4.93, Mn^{3+}/Mn^{2+} from 1.87 to 0.72, and Mn^{4+}/Mn^{2+} from 0.47 to 0.34. These changes indicate that Mn species improve charge redistribution by transferring electrons from Co to Mn, boosting catalytic efficiency [22]. Key factors contributing to the enhanced electrocatalytic activity,



Fig. 6. (a) SEM image and (b) HR-TEM image of $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF (the inset shows the intensity profile of corresponding areas) after long-term stability test. (c) Cyclic voltammograms of the Co^{2+}/Co^{3+} redox peak for designed catalysts, showing Co^{2+} to Co^{3+} transition, were measured over 10 cycles at 50 mV/s. (d) Electrochemical in situ Raman spectra of the $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF in the potential range of 0–1.70 V (vs. RHE). EIS Bode plots of (e) $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF and (f) Co(OH)₂-CoCo₂O₄/NF at the potentials of 0.95–1.65 V (vs. RHE). (g) Co 2*p*, (h) Mn 2*p*, and (i) Compare the surface molar ratios of Mn^{4+}/Mn^{2+} , Mn^{3+}/Mn^{2+} , Mn^{2+}/Mn^{0} , and Co^{3+}/Co^{2+} on $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF before and after long-term stability test using XPS.

stability, and water-splitting performance of Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF include: (I) Self-supported 2D/2D heterostructure: The nanowire arrays, coated with ultrathin nanosheets, create interconnected 3D porous channels that improve electrolyte penetration and oxygen diffusion. (II) Superhydrophilicity: The catalyst's superhydrophilic surface ensures close contact between electrolytes and active sites, accelerating mass and charge transfer at the interface and enhancing catalytic efficiency. (III) Electronic structure optimization: Oxygen vacancies adjust the electronic structure and conductivity, optimizing the adsorption energy of OER intermediates and accelerating reaction kinetics. (IV) Valence state modulation: Mn incorporation alters the valence state of adjacent Co atoms, increasing the Co³⁺/Co²⁺ ratio. The generated Co³⁺ species act as primary active sites, reducing activation energy for oxygencontaining intermediates and improving OER performance.

4. Conclusion

In summary, the Mn_{0.10}Co_{0.90}-CoCo₂O₄/NF catalyst exhibits exceptional OER and overall water-splitting performance, driven by its 2D/2D heterostructure, oxygen vacancies, and Mn-induced electronic modulation. Post-stability testing, SEM, and HR-TEM analyses confirmed the retention of the nanowire structure, with lattice spacing corresponding to active CoOOH. XPS analysis revealed an increased Co^{3+}/Co^{2+} ratio from 1.32 to 1.61, indicating enhanced active site exposure. Mn doping facilitated charge redistribution, as evidenced by reductions in Mn valence states. The catalyst demonstrated low overpotentials of 178 mV and 233 mV at 10 and 50 mA $\rm cm^{-2}$, respectively, along with a Tafel slope of 70.49 mV dec⁻¹, outperforming comparable systems. A high electrochemically active surface area (ECSA) of 10,398 cm² and minimal charge transfer resistance confirmed efficient electron transport. In situ Raman spectroscopy revealed the transformation of Co₃O₄ to CoOOH under operational conditions, identifying these as the active centers. Hydrophilicity analysis showed a zero-degree contact angle, ensuring optimal electrolyte penetration and mass transfer. Stability tests demonstrated sustained operation for over 280 h at 50 mA cm^{-2} , while water-splitting tests using a Pt/C cathode achieved a cell voltage of 1.70 V at 100 mA cm⁻² for 135 h. These findings highlight the synergistic effects of hierarchical design, oxygen vacancies, and Mn-Co interactions in enhancing conductivity, active site accessibility, and reaction kinetics. $Mn_{0.10}Co_{0.90}$ -CoCo₂O₄/NF emerges as a promising, cost-effective alternative for industrial water electrolysis.

CRediT authorship contribution statement

Tingting Tang: Writing – original draft, Data curation, Conceptualization. Yongle Chen: Methodology, Data curation. Kuoteng Sun: Investigation. Yanfang Teng: Formal analysis. Fengli Wei: Investigation. Tayirjan Taylor Isimjan: Writing – review & editing. Jingya Guo: Writing – review & editing. Jianniao Tian: Writing – review & editing. Xiulin Yang: Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2025.137314.

Data availability

The data that has been used is confidential.

References

- [1] Y. Li, A. Feng, L. Dai, B. Xi, X. An, S. Xiong, C. An, Progress on the design of electrocatalysts for large-current hydrogen production by tuning thermodynamic and kinetic factors, Adv. Funct. Mater. 34 (2024) 2316296, https://doi.org/ 10.1002/adfm.202316296.
- [2] P. De Luna, C. Hahn, D. Higgins, S.A. Jaffer, T.F. Jaramillo, E.H. Sargent, What would it take for renewably powered electrosynthesis to displace petrochemical processes? Science 364 (2019) 350–364. https://doi/abs/10.1126/science: aav3506.
- [3] M.M. Mohideen, B. Subramanian, J. Sun, J. Ge, H. Guo, A.V. Radhamani, S. Ramakrishna, Y. Liu, Techno-economic analysis of different shades of renewable and non-renewable energy-based hydrogen for fuel cell electric vehicles, Energy Strategy Rev. 174 (2023) 113153, https://doi.org/10.1016/j.rser.2023.113153.
- [4] L. Magnier, G. Cossard, V. Martin, C. Pascal, V. Roche, E. Sibert, I. Shchedrina, R. Bousquet, V. Parry, M. Chatenet, Fe–Ni-based alloys as highly active and lowcost oxygen evolution reaction catalyst in alkaline media, Nat. Mater. 23 (2024) 252–261, https://doi.org/10.1038/s41563-023-01744-5.
- [5] G. Li, G. Han, L. Wang, X. Cui, N.K. Moehring, P.R. Kidambi, D.-E. Jiang, Y. Sun, Dual hydrogen production from electrocatalytic water reduction coupled with formaldehyde oxidation via a copper-silver electrocatalyst, Nat. Commun. 14 (2023) 525, https://doi.org/10.1038/s41467-023-36142-7.
- [6] J. Song, Y. Chen, H. Huang, J. Wang, S.-C. Huang, Y.-F. Liao, A.E. Fetohi, F. Hu, H.-Y. Chen, L. Li, X. Han, K.M. El-Khatib, S. Peng, Heterointerface engineering of hierarchically assembling layered double hydroxides on cobalt selenide as efficient trifunctional electrocatalysts for water splitting and zinc-air battery, Adv. Sci. 9 (2022) 2104522, https://doi.org/10.1002/advs.202104522.
- [7] W. Liu, D. Zheng, T. Deng, Q. Chen, C. Zhu, C. Pei, H. Li, F. Wu, W. Shi, S.-W. Yang, Y. Zhu, X. Cao, Boosting electrocatalytic activity of 3d-block metal (hydro)oxides by ligand-induced conversion, Angew. Chem. Int. Ed. 60 (2021) 10614–10619, https://doi.org/10.1002/anie.202100371.
- [8] Z.-P. Wu, H. Zhang, S. Zuo, Y. Wang, S.L. Zhang, J. Zhang, S.-Q. Zang, X.W. Lou, Manipulating the local coordination and electronic structures for efficient electrocatalytic oxygen evolution, Adv. Mater. 33 (2021) 2103004, https://doi. org/10.1002/adma.202103004.
- [9] Z. Zhang, X. Liang, J. Li, J. Qian, Y. Liu, S. Yang, Y. Wang, D. Gao, D. Xue, Interfacial engineering of NiO/NiCo₂O₄ porous nanofibers as efficient bifunctional catalysts for rechargeable zinc–air batteries, ACS Appl. Mater. Interfaces 12 (2020) 21661–21669, https://doi.org/10.1021/acsami.0c03672.
- [10] N. Zhang, X. Feng, D. Rao, X. Deng, L. Cai, B. Qiu, R. Long, Y. Xiong, Y. Lu, Y. Chai, Lattice oxygen activation enabled by high-valence metal sites for enhanced water oxidation, Nat. Commun. 11 (2020) 4066, https://doi.org/10.1038/s41467-020-17934-7.
- [11] A. Moysiadou, S. Lee, C.-S. Hsu, H.M. Chen, X. Hu, Mechanism of oxygen evolution catalyzed by cobalt oxyhydroxide: cobalt superoxide species as a key intermediate and dioxygen release as a rate-determining step, J. Am. Chem. Soc. 142 (2020) 11901–11914, https://doi.org/10.1021/jacs.0c04867.
- [12] Y. Tian, X. Liu, L. Xu, D. Yuan, Y. Dou, J. Qiu, H. Li, J. Ma, Y. Wang, D. Su, S. Zhang, Engineering crystallinity and oxygen vacancies of Co(II) oxide nanosheets for high performance and robust rechargeable Zn–Air batteries, Adv. Funct. Mater. 31 (2021) 2101239, https://doi.org/10.1002/adfm.202101239.
- [13] H. Xue, A. Meng, T. Yang, Z. Li, C. Chen, Controllable oxygen vacancies and morphology engineering: Ultra-high HER/OER activity under base–acid conditions and outstanding antibacterial properties, J. Energy Chem. 71 (2022) 639–651, https://doi.org/10.1016/j.jechem.2022.04.052.
- [14] J. Béjar, F. Espinosa-Magaña, M. Guerra-Balcázar, J. Ledesma-García, L. Álvarez-Contreras, N. Arjona, L.G. Arriaga, Three-dimensional-order macroporous AB₂O₄ spinels (A, B =Co and Mn) as electrodes in Zn–Air batteries, ACS Appl. Mater. Interfaces 12 (2020) 53760–53773, https://doi.org/10.1021/acsami.0c14920.
- [15] X. Yang, Z. Zhou, Y. Zou, J. Kuang, D. Ye, S. Zhang, Q. Gao, S. Yang, X. Cai, Y. Fang, Interface reinforced 2D/2D heterostructure of Cu-Co oxides/FeCo hydroxides as monolithic multifunctional catalysts for rechargeable/flexible zincair batteries and self-powerld water splitting, Appl. Catal. B Environ. Energy 325 (2023) 122332, https://doi.org/10.1016/j.apcatb.2022.122332.
- [16] M.M. Mohideen, A. Qadir, B. Subramanian, S. Ramakrishna, Y. Liu, Nitrogen and sulfur incorporated chitosan-derived carbon sphere hybrid MXene as highly efficient electrocatalyst for oxygen reduction reaction, Mater. Today Phys. 46 (2024) 101528, https://doi.org/10.1016/j.mtphys.2024.101528.
- [17] Y. Wang, Y. Zhou, M. Han, Y. Xi, H. You, X. Hao, Z. Li, J. Zhou, D. Song, D. Wang, F. Gao, Environmentally-friendly exfoliate and active site self-assembly: thin 2D/ 2D heterostructure amorphous nickel–iron alloy on 2D materials for efficient oxygen evolution reaction, Small 15 (2019) 1805435, https://doi.org/10.1002/ smll.201805435.

- [18] K. Liu, H. Huang, Y. Zhu, S. Wang, Z. Lyu, X. Han, Q. Kuang, S. Xie, Edgesegregated ternary Pd–Pt–Ni spiral nanosheets as high-performance bifunctional oxygen redox electrocatalysts for rechargeable zinc–air batteries, J. Mater. Chem. A 10 (2022) 3808–3817, https://doi.org/10.1039/D1TA10585J.
- [19] S. Nagarani, G. Sasikala, M. Yuvaraj, R.D. Kumar, S. Balachandran, M. Kumar, ZnO-CuO nanoparticles enameled on reduced graphene nanosheets as electrode materials for supercapacitors applications, J. Energy Storage 52 (2022) 104969, https://doi.org/10.1016/j.est.2022.104969.
- [20] L. An, Z. Zhang, J. Feng, F. Lv, Y. Li, R. Wang, M. Lu, R.B. Gupta, P. Xi, S. Zhang, Heterostructure-promoted oxygen electrocatalysis enables rechargeable zinc–air battery with neutral aqueous electrolyte, J. Am. Chem. Soc. 140 (2018) 17624–17631, https://doi.org/10.1021/jacs.8b09805.
- [21] K. Zhu, F. Shi, X. Zhu, W. Yang, The roles of oxygen vacancies in electrocatalytic oxygen evolution reaction, Nano Energy 73 (2020) 104761, https://doi.org/ 10.1016/j.nanoen.2020.104761.
- [22] J. Li, X. Meng, X. Song, J. Qi, F. Liu, X. Xiao, Y. Du, G. Xu, Z. Jiang, S. Ye, S. Huang, J. Qiu, Valence engineering via manganese-doping on cobalt nitride nanoarrays for efficient electrochemically paired glycerol valorization and H₂ production, Adv. Funct. Mater. 34 (2024) 2316718, https://doi.org/10.1002/adfm.202316718.
- [23] M. Wang, L. Zhang, M. Huang, Q. Zhang, X. Zhao, Y. He, S. Lin, J. Pan, H. Zhu, One-step synthesis of a hierarchical self-supported WS₂ film for efficient electrocatalytic hydrogen evolution, J. Mater. Chem. A 7 (2019) 22405–22411, https://doi.org/10.1039/C9TA07868A.
- [24] C. Shan, Y. Zhang, Q. Zhao, J. Li, Y. Wang, R. Han, C. Liu, Q. Liu, New insight into opposite oxidation behavior in acetone and propane catalytic oxidation over CoMn based spinel oxides, Chem. Eng. J. 476 (2023) 146550, https://doi.org/10.1016/j. cej.2023.146550.
- [25] G. Janani, S. Surendran, H. Choi, M.-K. Han, U. Sim, In situ grown CoMn₂O₄ 3Dtetragons on carbon cloth: flexible electrodes for efficient rechargeable zinc–air battery powered water splitting systems, Small 17 (2021) 2103613, https://doi. org/10.1002/smll.202103613.
- [26] J. Lee, N. Son, N.-K. Park, H.-J. Ryu, J.-I. Baek, Y. Sohn, J.Y. Do, M. Kang, Electrochemical behavior of the flower shaped CoMn₂O₄ spinel structure assembled for effective HER from water splitting, Electrochim. Acta 379 (2021) 138168, https://doi.org/10.1016/j.electacta.2021.138168.
- [27] G. Mu, H. Xie, Y. Jian, Z. Jiang, L. Li, M. Tian, L. Zhang, J. Wang, S. Chai, C. He, Facile construction and enhanced catalytic activity of Co-Mn oxide with rich amorphous/crystalline interfaces for propane oxidation, Sep. Purif. Technol. 348 (2024) 127699, https://doi.org/10.1016/j.seppur.2024.127699.
- [28] C. Dong, C. Yang, Y. Ren, H. Sun, H. Wang, J. Xiao, Z. Qu, Local electron environment regulation of spinel CoMn₂O₄ induced effective reactant adsorption and transformation of lattice oxygen for toluene oxidation, Environ. Sci. Tech. 57 (2023) 21888–21897, https://doi.org/10.1021/acs.est.3c06782.
- [29] J. Reddy, M. Duraivel, K. Senthil, K. Prabakar, Kinetically controlled Mn doping effect on composition tuned CoMn hydroxide nanoflakes for overall water splitting application, ChemCatChem 14 (2022), https://doi.org/10.1002/cctc.202200966 e202200966.
- [30] H. Ding, C. Su, J. Wu, H. Lv, Y. Tan, X. Tai, W. Wang, T. Zhou, Y. Lin, W. Chu, X. Wu, Y. Xie, C. Wu, Highly crystalline iridium–nickel nanocages with subnanopores for acidic bifunctional water splitting electrolysis, J. Am. Chem. Soc. 146 (2024) 7858–7867, https://doi.org/10.1021/jacs.4c01379.
- [31] C. Tan, J. Chen, X.-J. Wu, H. Zhang, Epitaxial growth of hybrid nanostructures, Nat. Rev. Mater. 3 (2018) 17089, https://doi.org/10.1038/natrevmats.2017.89.
 [32] M.B. Askari, P. Salarizadeh, A. Beheshti-Marnani, S. Azizi, M.H. Ramezan Zadeh,
- [32] M.B. Askari, P. Salarizadeh, A. Beheshti-Marnani, S. Azizi, M.H. Ramezan Zadeh, T. Rohani, H. Beydaghi, H. Saeidfirozeh, Construction of MnCo₂O₄/rGO hybrid nanostructures as promising electrode material for high-performance pseudocapacitors, J. Mater. Sci. Mater. Electron. 32 (2021) 14863–14873, https:// doi.org/10.1007/s10854-021-06039-6.
- [33] T. Zhang, Z. Li, L. Wang, P. Sun, Z. Zhang, S. Wang, Spinel MnCo₂O₄ nanoparticles supported on three-dimensional graphene with enhanced mass transfer as an efficient electrocatalyst for the oxygen reduction reaction, ChemSusChem 11 (2018) 2730–2736, https://doi.org/10.1002/cssc.201801070.
 [34] S. Jung, R.A. Senthil, C.J. Moon, N. Tarasenka, A. Min, S.J. Lee, N. Tarasenko, M.
- [34] S. Jung, R.A. Senthil, C.J. Moon, N. Tarasenka, A. Min, S.J. Lee, N. Tarasenko, M. Y. Choi, Mechanistic insights into ZIF-67-derived Ir-doped Co₃O₄@N-doped carbon hybrids as efficient electrocatalysts for overall water splitting using in situ Raman spectroscopy, Chem. Eng. J. 468 (2023) 143717, https://doi.org/10.1016/j. cej.2023.143717.
- [35] S. Mo, Q. Zhang, J. Li, Y. Sun, Q. Ren, S. Zou, Q. Zhang, J. Lu, M. Fu, D. Mo, J. Wu, H. Huang, D. Ye, Highly efficient mesoporous MnO₂ catalysts for the total toluene oxidation: Oxygen-Vacancy defect engineering and involved intermediates using in situ DRIFTS, Appl. Catal. B Environ. Energy 264 (2020) 118464, https://doi.org/ 10.1016/j.apcatb.2019.118464.
- [36] C. Shan, Y. Zhang, Q. Zhao, K. Fu, Y. Zheng, R. Han, C. Liu, N. Ji, W. Wang, Q. Liu, Acid etching-induced in situ growth of λ-MnO₂ over CoMn spinel for lowtemperature volatile organic compound oxidation, Environ. Sci. Tech. 56 (2022) 10381–10390, https://doi.org/10.1021/acs.est.2c02483.
- [37] Y. Wang, T. Zhou, K. Jiang, P. Da, Z. Peng, J. Tang, B. Kong, W.-B. Cai, Z. Yang, G. Zheng, Reduced mesoporous Co₃O₄ nanowires as efficient water oxidation electrocatalysts and supercapacitor electrodes, Adv. Energy Mater. 4 (2014) 1400696, https://doi.org/10.1002/aenm.201400696.
- [38] P. Wang, J. Wang, X. An, J. Shi, W. Shangguan, X. Hao, G. Xu, B. Tang, A. Abudula, G. Guan, Generation of abundant defects in Mn-Co mixed oxides by a facile agargel method for highly efficient catalysis of total toluene oxidation, Appl. Catal. B Environ. Energy 282 (2021) 119560, https://doi.org/10.1016/j. apcatb.2020.119560.

- [39] X. Chen, Z. Zhang, S. Zhou, Y. Wei, S. Han, J. Jiang, In-situ growth transformation and oxygen vacancy synergistic modulation of the electronic structure of NiCo-LDH enables high-performance hybrid supercapacitors, Appl. Energy 371 (2024) 123670, https://doi.org/10.1016/j.apenergy.2024.123670.
- [40] Z. Wang, K. Xu, S. Ruan, C. He, L. Zhang, F. Liu, Mesoporous Co–Mn spinel oxides as efficient catalysts for low temperature propane oxidation, Catal. Lett. 152 (2022) 2695–2704, https://doi.org/10.1007/s10562-021-03839-7.
- [41] Y. Hu, Z. Luo, M. Guo, J. Dong, P. Yan, C. Hu, T.T. Isimjan, X. Yang, Interface engineering of Co₂N_{0.67}/CoMoO₄ heterostructure nanosheets as a highly active electrocatalyst for overall water splitting and Zn-H₂O cell, Chem. Eng. J. 435 (2022) 134795, https://doi.org/10.1016/j.cej.2022.134795.
- [42] H. Xiong, C. Du, Z. Ma, R. Zhi, S. Hao, X. Zhao, Z. Liu, F. Xu, H. Wang, Rational design of multiple heterostructures with synergistic effect for efficient and stable hydrogen evolution toward industrial alkaline water splitting, Adv. Funct. Mater. 34 (2024) 2402298, https://doi.org/10.1002/adfm.202402298.
- [43] C. Deng, K.-H. Wu, J. Scott, S. Zhu, R. Amal, D.-W. Wang, Ternary MnO/CoMn alloy@N-doped graphitic composites derived from a bi-metallic pigment as bifunctional electrocatalysts, J. Mater. Chem. A 7 (2019) 20649–20657, https://doi. org/10.1039/C9TA08016C.
- [44] H.-Y. Zhu, M.-T. Liu, G. Wang, R.-R. Du, H.-Y. Zhao, H. Lu, S.-Q. Yang, S. Tang, Z.-J. Guo, J. Yang, C.-Z. Zhu, F. Yang, Constructing core@shell structured photothermal nanosphere with thin carbon layer confined Co-Mn bimetals for pollutant degradation and solar interfacial water evaporation, Rare Met. 43 (2024) 1686–1701, https://doi.org/10.1007/s12598-023-02499-3.
- [45] S. Zhao, R. Jin, H. Abroshan, C. Zeng, H. Zhang, S.D. House, E. Gottlieb, H.J. Kim, J.C. Yang, R. Jin, Gold nanoclusters promote electrocatalytic water oxidation at the nanocluster/CoSe₂ interface, J. Am. Chem. Soc. 139 (2017) 1077–1080, https:// doi.org/10.1021/jacs.6b12529.
- [46] M.-R. Gao, X. Cao, Q. Gao, Y.-F. Xu, Y.-R. Zheng, J. Jiang, S.-H. Yu, Nitrogen-doped graphene supported CoSe₂ nanobelt composite catalyst for efficient water oxidation, ACS Nano 8 (2014) 3970–3978, https://doi.org/10.1021/nn500880v.
- [47] H. Zeng, M.H. Oubla, X. Zhong, N. Alonso-Vante, F. Du, Y. Xie, Y. Huang, J. Ma, Rational defect and anion chemistries in Co₃O₄ for enhanced oxygen evolution reaction, Appl. Catal. B Environ. Energy 281 (2021) 119535, https://doi.org/ 10.1016/j.apcatb.2020.119535.
- [48] N.C.S. Selvam, L. Du, B.Y. Xia, P.J. Yoo, B. You, Reconstructed water oxidation electrocatalysts: the impact of surface dynamics on intrinsic activities, Adv. Funct. Mater. 31 (2021) 2008190, https://doi.org/10.1002/adfm.202008190.
- [49] M.-Q. Yang, J. Wang, H. Wu, G.W. Ho, Noble metal-free nanocatalysts with vacancies for electrochemical water splitting, Small 14 (2018) 1703323, https:// doi.org/10.1002/smll.201703323.
- [50] Y. Yuan, S. Adimi, X. Guo, T. Thomas, Y. Zhu, H. Guo, G.S. Priyanga, P. Yoo, J. Wang, J. Chen, P. Liao, J.P. Attfield, M. Yang, A surface-oxide-rich activation layer (SOAL) on Ni₂Mo₃N for a rapid and durable oxygen evolution reaction, Angew. Chem. Int. Ed. 59 (2020) 18036–18041, https://doi.org/10.1002/ anie.202008116.
- [51] Y. Song, M. Sun, S. Zhang, X. Zhang, P. Yi, J. Liu, B. Huang, M. Huang, L. Zhang, Alleviating the work function of vein-like CoxP by Cr doping for enhanced seawater electrolysis, Adv. Funct. Mater. 33 (2023) 2214081, https://doi.org/10.1002/ adfm.202214081.
- [52] Z. Huang, M. Liao, S. Zhang, L. Wang, M. Gao, Z. Luo, T.T. Isimjan, B. Wang, X. Yang, Valence electronic engineering of superhydrophilic Dy-evoked Ni-MOF outperforming RuO₂ for highly efficient electrocatalytic oxygen evolution, J. Energy Chem. 90 (2024) 244–252, https://doi.org/10.1016/j. jechem.2023.11.012.
- [53] H.B. Tao, Y. Xu, X. Huang, J. Chen, L. Pei, J. Zhang, J.G. Chen, B. Liu, A general method to probe oxygen evolution intermediates at operating conditions, Joule 3 (2019) 1498–1509, https://doi.org/10.1016/j.joule.2019.03.012.
- [54] M. Xi, Z. Wu, Z. Luo, L. Ling, W. Xu, R. Xiao, H. Wang, Q. Fang, L. Hu, W. Gu, C. Zhu, Water activation for boosting electrochemiluminescence, Angew. Chem. Int. Ed. 62 (2023), https://doi.org/10.1002/anie.202302166 e202302166.
 [55] S. Zhao, Y. Wang, Y. Hao, L. Yin, C.-H. Kuo, H.-Y. Chen, L. Li, S. Peng, Lewis acid
- [55] S. Zhao, Y. Wang, Y. Hao, L. Yin, C.-H. Kuo, H.-Y. Chen, L. Li, S. Peng, Lewis acid driving asymmetric interfacial electron distribution to stabilize active species for efficient neutral water oxidation, Adv. Mater. 36 (2024) 2308925, https://doi.org/ 10.1002/adma.202308925.
- [56] S. Nagarani, J.-H. Chang, M. Yuvaraj, S. Balachandran, M. Kumar, S. Kanimozhi, Well-organized metal-free chemically reduced graphene oxide sheets as electrocatalysts for enhanced oxygen reduction reactions in alkaline media, Mater. Lett. 357 (2024) 135705. https://doi.org/10.1016/j.matlet.2023.135705.
- Lett. 357 (2024) 135705, https://doi.org/10.1016/j.matlet.2023.135705.
 [57] W. He, X. Tan, Y. Guo, Y. Xiao, H. Cui, C. Wang, Grain-boundary-rich RuO₂ porous nanosheet for efficient and stable acidic water oxidation, Angew. Chem. Int. Ed. (2024), https://doi.org/10.1002/anie.202405798 e202405798.
- [58] Y. Wang, A. Li, C. Cheng, Ultrathin Co(OH)₂ nanosheets@nitrogen-doped carbon nanoflake arrays as efficient air cathodes for rechargeable Zn–Air batteries, Small 17 (2021) 2101720, https://doi.org/10.1002/smll.202101720.
- [59] Y. Pan, K. Sun, Y. Lin, X. Cao, Y. Cheng, S. Liu, L. Zeng, W.-C. Cheong, D. Zhao, K. Wu, Z. Liu, Y. Liu, D. Wang, Q. Peng, C. Chen, Y. Li, Electronic structure and dband center control engineering over M-doped CoP (M = Ni, Mn, Fe) hollow polyhedron frames for boosting hydrogen production, Nano Energy 56 (2019) 411–419, https://doi.org/10.1016/j.nanoen.2018.11.034.
- [60] J. Wang, S. Xin, Y. Xiao, Z. Zhang, Z. Li, W. Zhang, C. Li, R. Bao, J. Peng, J. Yi, S. Chou, Manipulating the water dissociation electrocatalytic sites of bimetallic nickel-based alloys for highly efficient alkaline hydrogen evolution, Angew. Chem. Int. Ed. 61 (2022), https://doi.org/10.1002/anie.202202518 e202202518.
- [61] W.-K. Chong, B.-J. Ng, Y.J. Lee, L.-L. Tan, L.K. Putri, J. Low, A.R. Mohamed, S.-P. Chai, Self-activated superhydrophilic green ZnIn₂S₄ realizing solar-driven

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overall water splitting: close-to-unity stability for a full daytime, Nat. Commun. 14 (2023) 7676, https://doi.org/10.1038/s41467-023-43331-x.

- [62] Z. Wu, Y. Zhao, H. Wu, Y. Gao, Z. Chen, W. Jin, J. Wang, T. Ma, L. Wang, Corrosion engineering on iron foam toward efficiently electrocatalytic overall water splitting powered by sustainable energy, Adv. Funct. Mater. 31 (2021) 2010437, https:// doi.org/10.1002/adfm.202010437.
- [63] A.K. Shah, S. Bhowmick, D. Gogoi, N.R. Peela, M. Qureshi, Hollow cuboidal MnCo₂O₄ coupled with nickel phosphate: a promising oxygen evolution reaction electrocatalyst, Chem. Commun. 57 (2021) 8027–8030, https://doi.org/10.1039/ D1CC02383G.
- [64] N. Kalita, A. Sahu, S. Bhowmick, M. Qureshi, Synchronized redox pairs in metal oxide/hydroxide chemical analogues for an efficient oxygen evolution reaction, Chem. Commun. 58 (2022) 13747–13750, https://doi.org/10.1039/D2CC05225C.
- [65] J. Han, H. Wang, Y. Wang, H. Zhang, J. Li, Y. Xia, J. Zhou, Z. Wang, M. Luo, Y. Wang, N. Wang, E. Cortés, Z. Wang, A. Vomiero, Z.-F. Huang, H. Ren, X. Yuan, S. Chen, D. Feng, X. Sun, Y. Liu, H. Liang, Lattice oxygen activation through deep oxidation of Co₄N by Jahn–Teller–active dopants for improved electrocatalytic oxygen evolution, Angew. Chem. Int. Ed. 63 (2024), https://doi.org/10.1002/ anie.202405839 e202405839.
- [66] M. Zhao, J. Wang, C. Wang, Y. Sun, P. Liu, X. Du, H. Pan, H. Li, H. Liang, J. Guo, T. Ma, Enriched edge sites of ultrathin Ni₃S₂/NiO nanomeshes promote surface reconstruction for robust electrochemical water splitting, Nano Energy 129 (2024) 110020, https://doi.org/10.1016/j.nanoen.2024.110020.
- [67] P. Gao, Y. Zeng, P. Tang, Z. Wang, J. Yang, A. Hu, J. Liu, Understanding the synergistic effects and structural evolution of Co(OH)₂ and Co₃O₄ toward boosting electrochemical charge storage, Adv. Funct. Mater. 32 (2022) 2108644, https:// doi.org/10.1002/adfm.202108644.
- [68] H. Su, W. Zhou, W. Zhou, Y. Li, L. Zheng, H. Zhang, M. Liu, X. Zhang, X. Sun, Y. Xu, F. Hu, J. Zhang, T. Hu, Q. Liu, S. Wei, In-situ spectroscopic observation of dynamiccoupling oxygen on atomically dispersed iridium electrocatalyst for acidic water oxidation, Nat. Commun. 12 (2021) 6118, https://doi.org/10.1038/s41467-021-26416-3.
- [69] Y. Zhu, Q. Qian, Y. Chen, X. He, X. Shi, W. Wang, Z. Li, Y. Feng, G. Zhang, F. Cheng, Biphasic transition metal nitride electrode promotes nucleophile oxidation reaction for practicable hybrid water electrocatalysis, Adv. Funct. Mater. 33 (2023) 2300547, https://doi.org/10.1002/adfm.202300547.