

Article

Oxygen Vacancy and Heteroatom Co-Engineering in WO₃@Mn₂WO₄ Core–Shell Nanostructures for Advanced Tungsten-Based Electrocatalysis

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Abstract

Tungsten-based electrocatalysts are considered promising alternatives to noble metal catalysts for electrochemical water splitting; however, their practical application is severely limited by inherently sluggish reaction kinetics and low density of active sites. In this study, a rationally designed Co-doped WO₃@Mn₂WO₄ core–shell nanostructure with oxygen vacancy modulation (Co-WO₃@Mn₂WO₄-0.6-O_v) was fabricated via a facile hydrothermal synthesis combined with post-treatment using borohydride reduction. By precisely tuning the Co doping concentration (0, 0.3, 0.6, and 0.9 mM), the optimal catalytic performance was identified. Structural characterization confirmed the successful construction of the core–shell heterostructure and the effective modulation of the electronic structure of the W/Mn active sites through Co doping and oxygen vacancy engineering. Electrochemical measurements demonstrated that the optimized Co-WO₃@Mn₂WO₄-0.6-O_v catalyst exhibits a Tafel slope as low as 53.8 mV dec^{−1} for the hydrogen evolution reaction (HER) under acidic condition of 0.5 M H₂SO₄, achieving the best performance among all prepared samples and reflecting significantly accelerated electrocatalytic kinetics. This synergistic strategy combining heteroatom doping and oxygen vacancy engineering is also applicable to overall water splitting, enabling a membrane electrode assembly to achieve excellent long-term stability for over 40 h in both acidic and alkaline media. The enhanced catalytic performance is attributed to the synergistic effects of Co doping, oxygen vacancies, and the core–shell structure, which collectively promote interfacial charge transfer and increase the exposure of active sites.

Keywords: tungsten-based electrocatalyst; Co doping; oxygen vacancy; core shell heterostructure; overall water splitting; electrocatalysis



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1. Introduction

The growing of the global energy crisis and the worsening of environmental pollution have propelled the advancement of clean and sustainable energy conversion technologies [1,2]. Electrochemical water splitting has garnered considerable interest for its capacity to effectively generate high-purity hydrogen, comprising two half-reactions: the HER and

the oxygen evolution reaction (OER) [3–5]. Nonetheless, the OER is constrained by the slow kinetics of the inherent four-electron transfer process, whereas the HER under acidic conditions encounters difficulties including high overpotential and inadequate catalyst stability [6,7]. These disadvantages result in elevated energy consumption and diminished efficiency, thereby limiting practical applications [8].

Noble metal catalysts such as Pt/C, IrO₂, and RuO₂ demonstrate exceptional electrocatalytic efficacy; yet, their scarcity, exorbitant cost, and inadequate stability under extreme conditions significantly impede their commercialisation [9,10]. Consequently, the advancement of economical, highly efficient, and stable non-noble metal electrocatalysts has emerged as an essential research need [11]. Tungsten-based materials, especially WO₃ composites, have emerged as viable options owing to their modifiable structure, robust corrosion resistance, and affordability [12–14]. Nonetheless, traditional WO₃ catalysts continue to exhibit deficiencies in intrinsic activity, active site density, conductivity, and kinetics, particularly in acidic environments [15]. To address these difficulties, techniques including heteroatom doping, oxygen vacancy engineering, and heterostructure construction have demonstrated efficacy in modifying electronic structures, enhancing active site exposure, and facilitating charge transfer [16–18].

In this work, we report a pronounced strategy that synergistically integrates Co heteroatom doping, oxygen vacancy engineering, and core shell heterostructure construction to fabricate cobalt-doped WO₃@Mn₂WO₄ core shell nanostructures rich in oxygen vacancies (Co-WO₃@Mn₂WO₄-0.6-O_v) via hydrothermal synthesis combined with borohydride reduction. By precisely tuning the Co doping concentration (0, 0.3, 0.6, and 0.9 mM) and subsequently introducing abundant surface oxygen vacancies into the optimal sample, we are able to distinguish and clarify the independent modulation effects of Co doping and oxygen vacancies on the electronic structure of W/Mn active sites and the resulting hydrogen evolution performance. This synergistic strategy simultaneously addresses the inherent drawbacks of conventional tungsten-based electrocatalysts, including low intrinsic activity and severe dissolution/corrosion under alkaline environments, thereby achieving efficient and stable hydrogen evolution catalysis in both acidic and alkaline electrolytes. The optimized Co-WO₃@Mn₂WO₄-0.6-O_v catalyst exhibits remarkable electrocatalytic performance, delivering an HER overpotential of 61.4 mV at a cathodic current density of 5 mA cm^{−2} with a Tafel slope of 85.1 mV dec^{−1} in 1 M KOH aqueous solution. When assembled into a membrane electrode assembly for overall water splitting tests, the catalyst displays long-term durability over 40 h. This study proposes a feasible strategy to boost the electrocatalytic performance of tungsten-based catalysts and offers valuable insights for the rational design of non-noble metal electrocatalysts toward sustainable energy conversion applications.

2. Experiments

2.1. Preparation of WO₃ Nanorods

In a typical hydrothermal system, 4 mmol of sodium tungstate and graded cobalt nitrate (0, 0.3, 0.6, 0.9 mM) were dissolved in 60 mL of deionized water. Next, 4 g sodium sulfate and 1 g oxalic acid were introduced into the above solution, and the mixture was magnetically stirred for 0.5 h at room temperature to form a homogeneous tungsten-containing precursor solution.

Pretreated carbon cloth substrates were fully immersed in the precursor solution, then the whole mixture was sealed in a Teflon-lined autoclave and maintained at 180 °C for 6 h for in-situ crystal growth. After the autoclave cooled naturally to ambient temperature, the carbon cloth loaded with tungsten oxide crystalline precursors was rinsed alternately with ethanol and deionized water, followed by drying at 60 °C for 8 h and calcination at 350 °C

for 2 h in a muffle furnace. After heat treatment, uniform polyhedral tungsten trioxide particles grow on the surface of carbon cloth.

2.2. Preparation of Co-WO₃@Mn₂WO₄ Core Shell Structure

The as-prepared carbon cloth-supported WO₃ octahedral polyhedral particles were immersed in a solution consisting of 0.7902 g of potassium permanganate, 2 mL of sulfuric acid and 50 mL of deionized water, and then heated in an oven at 80 °C for 50 min. The prepared product was washed several times with ethanol and distilled water, respectively, and dried at 60 °C for 4 h. Finally, the sample was annealed in air at 400 °C for 30 min.

2.3. Preparation of Co-WO₃@Mn₂WO₄-0.6-O_v with Oxygen Vacancies

The carbon cloth of Co-WO₃@Mn₂WO₄ with a cobalt doping concentration of 0.6 mM was immersed in a freshly prepared 0.2 mol/L sodium borohydride aqueous solution and magnetically stirred at room temperature for 30 min to introduce abundant surface oxygen vacancies. After the reduction treatment, the sample was thoroughly washed with anhydrous ethanol and deionized water to remove residual reducing agent, then dried at 60 °C for 4 h to obtain Co-WO₃@Mn₂WO₄ catalyst.

2.4. Structural and Morphological Characterizations

In this study, various characterization techniques were adopted. The X-ray diffractometer (XRD, D/max 2500, Rigaku Corporation, Tokyo, Japan) and X-ray photoelectron spectrometer (XPS, ESCALAB 250, Thermo Fisher Scientific, Hillsboro, OR, USA) equipped with an Al K α radiation source were used to analyze the crystal structure and chemical composition of the samples, respectively. The Hitachi SU8020 scanning electron microscope (SEM, Hitachi High-Tech Corporation, Tokyo, Japan) and FEI Talos F200X transmission electron microscope (TEM, Thermo Fisher Scientific, Hillsboro, OR, USA) were utilized to observe the morphology and microstructure of the materials.

(1) XRD characterization

XRD characterization of carbon cloth-supported catalysts used Cu K α radiation ($\lambda = 0.15406$ nm), scanning 20° to 70° at 5° min⁻¹. Catalyst-loaded carbon cloth slices were flattened on glass slides before testing. Patterns were matched with WO₃ (PDF#33-1387) and Mn₂WO₄ (PDF#10-0447) standard cards. Peak alignment verified successful WO₃@Mn₂WO₄ heterostructure, proving Co doping and oxygen vacancy regulation did not introduce no impurity crystal phases.

(2) XPS characterization

X-ray photoelectron spectroscopy with an Al K α excitation source was applied to analyze the surface elemental composition, chemical valence states and oxygen vacancy species of carbon cloth-based catalysts. The C 1s peak at 284.8 eV calibrated all binding energies to remove charge shift interference. Full survey spectra and high-resolution narrow spectra of O 1s, Mn 2p, W 4f and Co 2p were collected. O 1s spectra were split into lattice oxygen O1, vacancy-related defective oxygen O2 and adsorbed surface oxygen O3, and O2's relative area ratio qualitatively was used to qualitatively estimate vacancy concentrations. Mn 2p, W 4f and Co 2p were fitted using standard spin orbit doublets plus satellite peaks to expose electronic redistribution at Mn/W sites caused by Co doping and oxygen vacancies. Every carbon cloth sample was fixed on conductive carbon tape before XPS characterization.

(3) FE-SEM characterization

Field-emission scanning electron microscopy was used to characterize catalyst morphology, crystal dispersion, nanoparticle distribution, agglomeration and core shell in-

interface. Carbon cloth samples were mounted on conductive tape and gold-sputtered to boost conductivity and avoid charging effects. Low-magnification SEM assessed uniformity of samples with 0.3, 0.6 and 0.9 mM Co doping, while high-magnification views tracked nanoparticle dispersion and interfacial adhesion. Morphology comparison between original Co-WO₃@Mn₂WO₄ and reduced Co-WO₃@Mn₂WO₄-0.6-O_v proved oxygen vacancy tuning optimizes hierarchical structure, raises specific surface area and builds electrolyte/gas transport pathways for electrocatalysis.

2.5. Electrochemical Performance Measurements

Carbon cloth was selected as the conductive substrate for supporting catalysts in this experiment. Prior to catalyst growth, carbon cloth substrates were ultrasonically cleaned in ethanol and deionized water for 15 min each to eliminate surface organic contaminants and grease, followed by overnight drying in an oven at 60 °C. The catalyst-grown carbon cloth was cut into 1 cm × 1 cm slices to serve as working electrodes.

All three-electrode electrochemical measurements were performed at room temperature and atmospheric pressure. The working electrodes included carbon cloth loaded with pure WO₃, Co-WO₃@Mn₂WO₄, and the 0.6 mM sample treated with sodium borohydride; a platinum plate and saturated KCl Ag/AgCl electrode were used as counter and reference electrodes, respectively. The electrolyte for alkaline systems was 1 mol/L aqueous KOH solution, while the electrolyte for acidic systems is 0.5 mol/L aqueous H₂SO₄ solution. Identical electrode preparation procedures and the DH660 electrochemical workstation were adopted for all samples to guarantee fair comparison of electrocatalytic performance.

By collecting cyclic voltammetry (CV) curves at various scan rates within the non-faradaic potential window where no redox reactions occur, the double-layer capacitance C_{dl} can be calculated to evaluate the electrochemically active surface area (ECSA) of each catalyst. For the linear fitting plot derived from CV data, the vertical axis represents the current density difference Δj in units of mA cm⁻², and the horizontal axis denotes the scan rate V with units of mV s⁻¹. The slope obtained from linear fitting between Δj and scan rate is defined as the double-layer capacitance C_{dl}, which is uniformly reported in mF cm⁻². The formula for calculating the electrochemically active surface area is shown below:

$$\text{ECSA} = C_{dl}/C_s$$

where C_{dl} stands for the double-layer capacitance acquired from linear fitting; C_s = 0.04 mF cm⁻² refers to the standard specific capacitance of a flat metal oxide surface.

3. Results and Discussion

3.1. Structural and Morphological Analysis

The as-prepared WO₃@Mn₂WO₄ is an in-situ grown core shell heterostructure on carbon cloth, rather than a physical mixture of pure phases. Minor mismatches in peak intensity and slight 2 θ shifts stem from interfacial lattice strain, crystal preferred orientation of polyhedral particles, and lattice defects induced by Co doping and oxygen vacancies. All major diffraction peaks match WO₃ (PDF#33-1387) and Mn₂WO₄ (PDF#10-0447) without impurity signals, confirming successful heterostructure construction [19–21]. The symbols above peaks near 2 θ = 30° denote standard Mn₂WO₄ reference positions to highlight the matching of its characteristic (220) peak.

Initially, Figure 1a presents the crystal structure of the synthesised WO₃@Mn₂WO₄-based catalysts, which was examined using X-ray diffraction (XRD). All distinctive diffraction peaks of the samples are accurately correlated with the standard cards of WO₃ (PDF#33-1387) and Mn₂WO₄ (PDF#10-0447). No impurity peaks are detected in any sample, thereby

validating the effective synthesis of the high-purity $\text{WO}_3@\text{Mn}_2\text{WO}_4$ heterostructure [22,23]. The incorporation of Co doping and oxygen vacancies does not affect the primary crystal phase, confirming the structural stability of the improved catalysts [24]. Thereafter, the surface elemental composition of the catalysts was analysed using comprehensive X-ray photoelectron spectroscopy (XPS), as illustrated in Figure 1b. The survey spectrum of the pristine $\text{WO}_3@\text{Mn}_2\text{WO}_4$ sample distinctly displays typical peaks corresponding to Mn 2p, O 1s, C 1s, and W 4f, aligning with the anticipated elemental constituents of the material [25]. Significantly, further well-defined Co 2p signals are observed in the Co- $\text{WO}_3@\text{Mn}_2\text{WO}_4-0.6-\text{O}_v$ sample, offering direct confirmation of the successful integration of Co dopants into the catalyst structure.

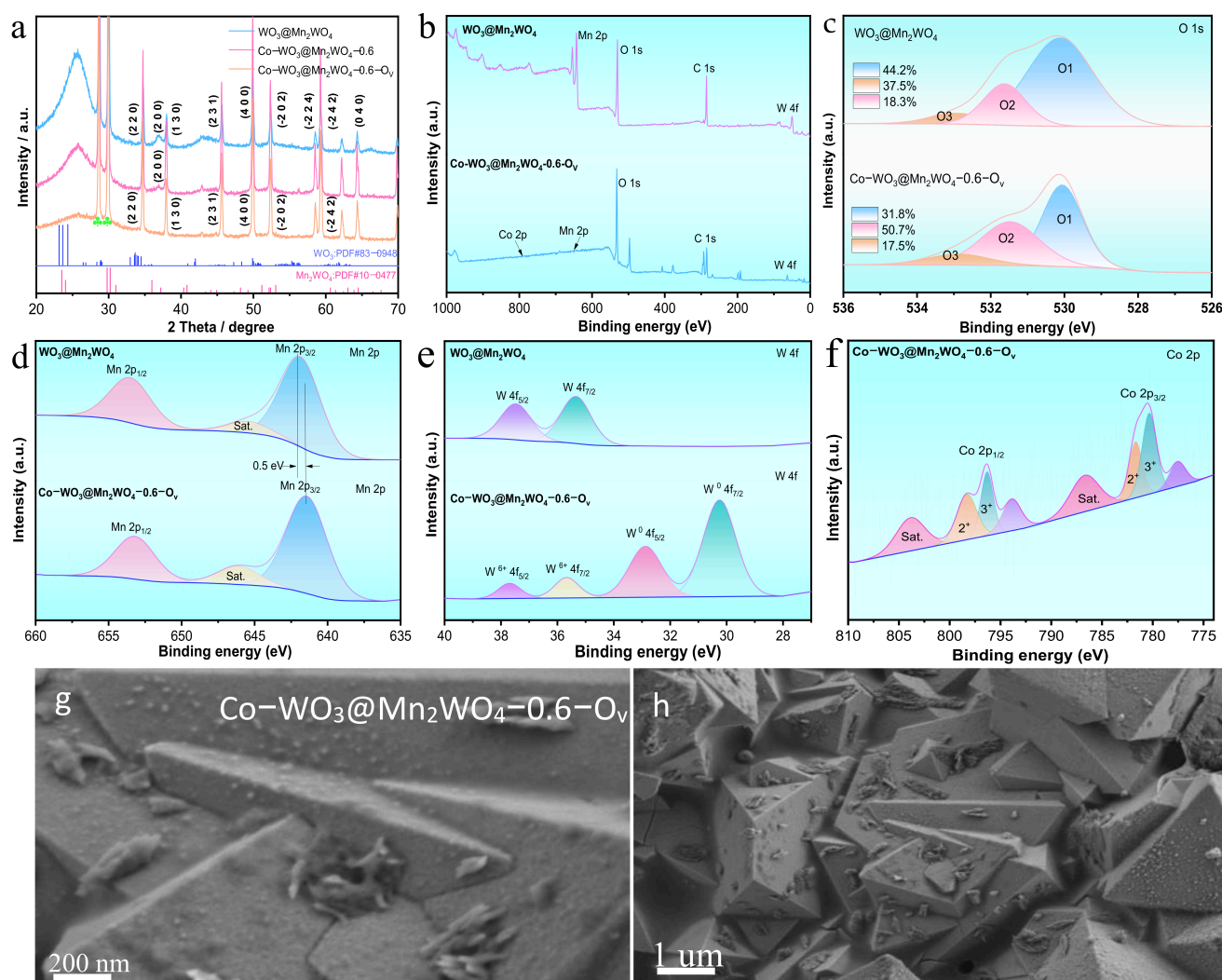


Figure 1. (a) XRD patterns, (b) full XPS survey, (c–f) high-resolution O 1s, Mn 2p, W 4f, Co 2p XPS spectra, and (g,h) SEM images of the as-prepared $\text{WO}_3@\text{Mn}_2\text{WO}_4$ -based catalysts with Co doping and oxygen vacancies.

High-resolution O 1s X-ray photoelectron spectroscopy (XPS) was performed to analyze the surface oxygen species of the as-prepared catalysts (Figure 1c). The O 1s envelopes of both pristine $\text{WO}_3@\text{Mn}_2\text{WO}_4$ and $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4-0.6-\text{O}_v$ are deconvoluted into three characteristic subpeaks assigned to lattice oxygen (O1), vacancy-associated defective oxygen (O2), and surface adsorbed hydroxyl/water oxygen (O3), respectively. As quantified in Figure 1c, the atomic proportion of defective oxygen (O2) rises sharply from 37.5% for pristine $\text{WO}_3@\text{Mn}_2\text{WO}_4$ to 50.7% for $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4-0.6-\text{O}_v$ after Co doping and

borohydride reduction treatment. Although O2 becomes the dominant oxygen component in the vacancy-rich sample, lattice oxygen (O1) still maintains a considerable atomic percentage of 31.8%, which verifies that the bulk crystalline core shell heterostructure remains intact without severe surface amorphization or full phase collapse. The prominent redistribution of three oxygen species alters the overall electronic state of surface sites, which accounts for the noticeable binding energy shift of the O 1s spectrum observed for Co-WO₃@Mn₂WO₄-0.6-O_v. Local electronic rearrangement triggered by abundant surface oxygen vacancies optimizes the exposure of catalytic active sites, which firmly demonstrates the successful introduction of oxygen vacancy defects via the proposed modification strategy. To thoroughly examine the modulation effect of cobalt doping and oxygen vacancies on the electronic structure of manganese active sites, high-resolution manganese 2p X-ray photoelectron spectroscopy (XPS) spectra of the samples were obtained, as illustrated in Figure 1d. The Mn 2p spectra of both samples are analysed using the distinctive Mn 2p_{3/2} and Mn 2p_{1/2} peaks, together with satellite peaks, which correspond to the unique valence state of Mn²⁺ [26–28]. In comparison to the pristine WO₃@Mn₂WO₄, the Mn 2p_{3/2} peak of the Co-WO₃@Mn₂WO₄-0.6-O_v sample exhibits a shift to a lower binding energy of 0.5 eV, indicating that the modification successfully modulates the electron cloud density of Mn atoms and enhances the electronic structure of the active sites. Oxygen vacancies are generated in the outer Mn₂WO₄ shell, while Co dopant atoms reside within the inner WO₃ core. The potential barrier at the core shell interface hinders long-distance migration of electrons released by surface vacancies toward internal Co sites. Mn species distributed in the outer shell possess abundant empty 3d orbitals, which can capture excess electrons liberated from oxygen vacancies and induce a negative shift in the binding energy of Mn 2p_{3/2}. Only a small fraction of electrons can tunnel through the interface to partially reduce W⁶⁺ into W⁵⁺/W⁴⁺, which is consistent with the results of the W 4f spectra. Figure 1e illustrates high-resolution W 4f X-ray photoelectron spectroscopy (XPS) measurements conducted on the samples to investigate the impact of alteration on the valence state of the W element [29,30]. The W 4f spectrum of the pristine WO₃@Mn₂WO₄ sample exclusively exhibits the distinctive W 4f_{5/2} and W 4f_{7/2} peaks of W⁶⁺, signifying that W consistently occurs in the +6 valence state. Conversely, in addition to W⁶⁺, low-valence tungsten species, including W⁵⁺ and W⁴⁺ (denoted as W⁰), are also detected in Co-WO₃@Mn₂WO₄-0.6-O_v sample, confirming that the inclusion of oxygen vacancies facilitates the partial reduction of W and enhances the valence diversity of active sites [31]. Figure 1f presents the high-resolution Co 2p XPS spectrum of Co-WO₃@Mn₂WO₄-0.6-O_v material. Two typical spin orbit split main peaks appear at 781 eV (Co 2p_{3/2}) and 796 eV (Co 2p_{1/2}), and each main peak can be deconvoluted into two sub-peaks corresponding to low-valence Co²⁺ and high-valence Co³⁺. Distinct satellite peaks at 787 eV and 804 eV confirm that doped cobalt exists in an oxidized state instead of metallic cobalt. Fitting results verify the coexistence of Co²⁺ and Co³⁺ species. Abundant surface oxygen vacancies generated by sodium borohydride reduction significantly raise the relative content of Co²⁺, which reveals that oxygen vacancies can tune the local electronic environment of cobalt ions and facilitate the partial reduction of Co³⁺ to Co²⁺. To quantitatively analyze the variation in surface elemental composition of materials before and after Co doping and oxygen vacancy construction, we summarize the atomic percentage of each element measured by full-range XPS spectra into the pie charts in Figure S1, and these results can indirectly verify the core shell structural characteristics of the as-prepared composite.

As presented in Figure S1a for the pristine WO₃@Mn₂WO₄ substrate, only C, O, Mn and W signals are detected on the material surface, with the atomic percentage of surface tungsten as low as merely 0.23%. Notably, no Co signal is captured for the blank sample, indicating the absence of cobalt species on the outer surface of the undoped substrate. In

sharp contrast, the Co-WO₃@Mn₂WO₄-0.6-O_v sample (Figure S1b) exhibits a Co atomic percentage of 0.73% on its surface, accompanied by a dramatic rise in surface oxygen content from 38.53% to 62.31%. Although the surface W atomic ratio slightly increases to 0.47%, it remains at an extremely low level overall. The distinct differences in elemental contents mentioned above sufficiently demonstrate that Co dopant species and abundant oxygen vacancies are successfully modified on the outer shell layer of the material, while tungsten-containing phases are encapsulated within the inner core region.

Thereafter, the micromorphology and structural attributes of Co-WO₃@Mn₂WO₄-0.6-O_v were extensively analysed utilising scanning electron microscopy (SEM). Figure 1g presents a high-magnification SEM image of Co-WO₃@Mn₂WO₄-0.6-O_v, which distinctly illustrates that the material exhibits a polyhedral crystal structure characterised by a smooth crystalline surface and pronounced sharp edges [32]. A substantial quantity of fine nanoparticles is uniformly distributed on the surface, validating the successful formation of the heterostructure and robust interfacial contact. This offers adequate active sites and effective electron transport routes for catalytic processes. Figure 1h displays the low-magnification SEM picture, clearly illustrating the sample's general morphological characteristics. The material displays a polyhedral crystal structure characterised by uniform dimensions, exceptional dispersibility, and the absence of significant agglomeration, hence confirming its superior structural integrity and homogeneity [33–35]. This distinctive hierarchical structure not only enhances the specific surface area of the material but also offers many pathways for electrolyte infiltration and gas diffusion, establishing a robust structural foundation for the catalyst's superior electrocatalytic performance.

To further highlight the outstanding bifunctional water-splitting activity of Co-WO₃@Mn₂WO₄-0.6-O_v, we systematically compare its HER and OER electrochemical parameters with state-of-the-art tungsten-based electrocatalysts in Tables S1 and S2 under alkaline and acidic electrolytes. For HER, our catalyst merely requires 61.4 mV (1.0 M KOH) and 124 mV (0.5 M H₂SO₄) overpotential to reach 10 mA cm⁻², greatly exceeding Ni_{0.4}WO_{3-x}S_x, WS₂/WO_{3-x}-2, WO₃/CoP and W-NiCo₂O₄. In alkaline OER tests, it delivers a low overpotential of 350.6 mV paired with a small Tafel slope of 65 mV dec⁻¹, outperforming Ni_{0.4}WO_{3-x}S_x, WO₃/CoP and Mn-WO₃. Although W-Ni₂P NS/CC holds a slightly lower OER overpotential, its much larger Tafel slope indicates far slower catalytic kinetics. These cross-reference comparisons fully verify that Co doping combined with oxygen vacancy construction synergistically optimizes the material electronic configuration, accelerates interfacial charge transport and boosts both HER and OER reaction, making this core shell heterostructure superior to most previously reported tungsten-based electrocatalysts.

Figure 2a–f systematically examine the influence of Co doping levels on the catalyst micromorphology. SEM characterisations were conducted on three materials with varying Co doping ratios: Co-WO₃@Mn₂WO₄-0.3, -0.6, and -0.9. Figure 2a,c,e represent high-magnification SEM pictures, whereas Figure 2b,d,f depict the comparable low-magnification SEM images. The low-magnification morphologies reveal that all samples exhibit rather uniform polyhedral crystal structures with excellent dispersibility and no significant agglomeration, suggesting that varying Co doping levels do not compromise the primary morphology of the material [36–38]. The high-magnification photos distinctly demonstrate significant variations in the surface nanostructures: the Co-WO₃@Mn₂WO₄-0.3 sample demonstrates a sparse particle dispersion, significant agglomeration, and inadequate interfacial bonding [39]. The over-doped Co-WO₃@Mn₂WO₄-0.9 sample exhibits significant particle aggregation and an irregular size distribution. Conversely, the Co-WO₃@Mn₂WO₄-0.6 sample features uniformly dispersed nanoparticles of moderate size and strong interfacial contact, which guarantees enough exposure of active sites and promotes swift electron and mass transport. These morphological findings further validate that

0.6 is the best cobalt doping ratio, which aligns closely with the conclusions drawn from crystal structure and electronic state investigations. Comparing the micromorphologies of $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.6}$ and $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.6-O}_v$ (Figure 1g,h) reveals that the optimised sample, following the introduction of oxygen vacancies, displays a more uniform distribution of surface nanoparticles, devoid of significant agglomeration, along with intact crystal edges and enhanced interfacial contact. This microstructure, optimised by oxygen vacancies, enhances the specific surface area of the material, efficiently exposes additional active sites, accelerates electron transfer efficiency, and facilitates electrolyte penetration and gas diffusion. This effectively rectifies the deficiencies of the oxygen vacancy-free sample, such as facile particle aggregation, inadequate utilisation of active sites, and sub-optimal mass transfer efficiency. The $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.6-O}_v$ sample offers essential structural support for its superior electrocatalytic activity, hence confirming the efficacy of the synergistic modification technique using “Co doping and oxygen vacancies”.

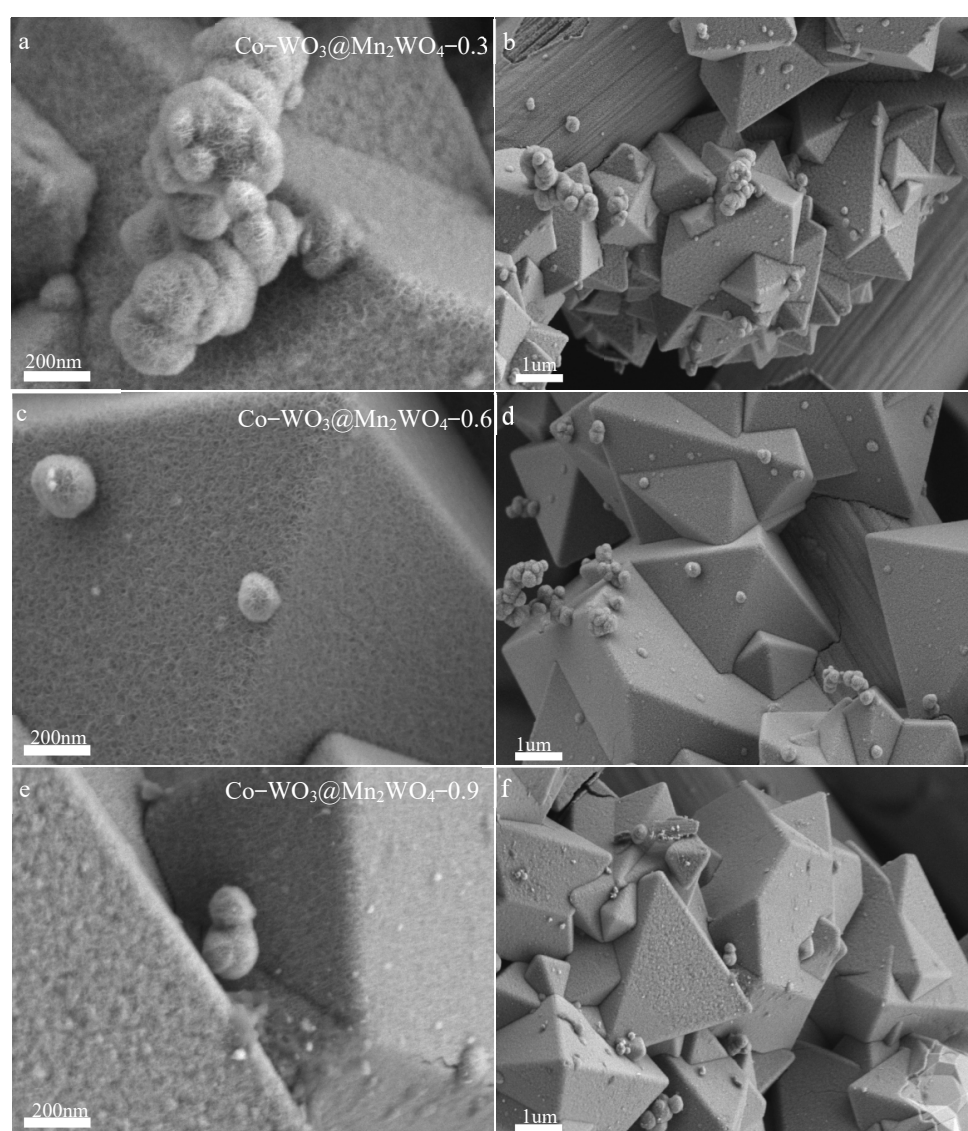


Figure 2. (a) High-magnification SEM image of the $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.3}$ sample; (b) Low-magnification SEM image of the $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.3}$ sample; (c) High-magnification SEM image of the $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.6}$ sample; (d) Low-magnification SEM image of the $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.6}$ sample; (e) High-magnification SEM image of the $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.9}$ sample; (f) Low-magnification SEM image of the $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.9}$ sample.

3.2. Electrochemical Performance Analysis

Before exploring the performance improvement induced by oxygen vacancy construction, we first systematically investigated the influence of Co doping concentration on the intrinsic electrocatalytic activity of $\text{WO}_3@\text{Mn}_2\text{WO}_4$. Three vacancy-free catalysts with Co concentrations of 0.3, 0.6 and 0.9 mM were fabricated for primary performance screening. At a low Co loading of 0.3 mM, the limited number of Co-derived active sites restricts the HER and OER catalytic activity. When Co concentration reaches 0.6 mM, well-distributed Co dopants tune the electronic structure of the host material, create abundant $\text{Co}^{2+}/\text{Co}^{3+}$ heterovalent interfaces and greatly increase the accessible active sites, leading to outstanding bifunctional catalytic activity for overall water splitting. In contrast, excessive Co doping at 0.9 mM causes severe aggregation of cobalt species, obstructs mass transfer pathways and accelerates charge recombination, which deteriorates the catalytic kinetics.

According to the above screening results, the 0.6 mM Co-doped sample with the best intrinsic performance was chosen to introduce surface oxygen vacancies. Such design allows us to separately reveal the modulation effect of oxygen vacancies and avoid the overlapping interference of mismatched Co doping ratios, so that we can clearly separate the independent contributions of Co doping and oxygen vacancy engineering to electrocatalysis.

This study initially assessed the electrocatalytic efficacy of several catalysts for the HER. Figure 3a illustrates the HER linear sweep voltammetry (LSV) curves for each sample in an alkaline electrolyte. Within the potential range of 0.25 to 0 V, the current density of all samples increases as the applied potential decreases. Significant changes in HER catalytic activity are detected when comparing the several curves: the $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.6-O}_v$ sample displays the most negative cathodic current density throughout the whole potential range, suggesting it can facilitate a greater HER rate at the same potential, hence showcasing a significant catalytic activity advantage. Conversely, the pure-phase $\text{WO}_3@\text{Mn}_2\text{WO}_4$ sample exhibits a current density approaching zero, indicating the weakest catalytic reaction. The other samples, $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.3}$ and $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.6}$, exhibit HER activity that falls between these two extremes. The preliminary LSV results indicate that Co doping and subsequent oxygen vacancy engineering significantly influence the HER activity of the catalysts, with $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.6-O}_v$ and $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.9}$ exhibiting the highest HER catalytic potential. Figure 3b illustrates the respective potentials of each sample at current densities of -5, -10, and -15 mA cm^{-2} to further quantify and validate the differences in activity. The results indicate that at all three current density conditions, $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.6-O}_v$ exhibits the lowest overpotentials of 61.4, 146.4, and 226.4 mV, whilst $\text{WO}_3@\text{Mn}_2\text{WO}_4$ displays the highest overpotential of 344.5 mV. This result aligns completely with the trend noted in the LSV curves, further validating the HER activity superiority of $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.6-O}_v$ based on essential performance measures.

Figure 3c elucidates the HER kinetics for each sample through Tafel plots. $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.6-O}_v$ exhibits the lowest Tafel slope of 85.1 mV dec^{-1} among all samples, signifying the most rapid reaction kinetics. Conversely, $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.3}$ displays a slope of 231.2 mV dec^{-1} , signifying markedly sluggish kinetics. Tafel analysis indicates that cobalt doping and oxygen vacancy engineering significantly diminish the kinetic resistance of the reaction, hence facilitating the superior HER activity of $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.6-O}_v$. Subsequently, Figure 3d illustrates the HER double-layer capacitance (C_{dl}) test curves for several electrocatalysts. The findings reveal that $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.6-O}_v$ displays a linear slope of 0.00535 mF cm^{-2} , the highest among all samples, indicating it has the greatest electrochemically active surface area on the HER side and can reveal more effective catalytic sites. Conversely, the slope of $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-0.3}$ is markedly reduced, signifying inadequate accessibility of active sites. This outcome, from the fundamental

viewpoint of active site density, elucidates the rationale for the superior catalytic efficacy of Co-WO₃@Mn₂WO₄-0.6-O_v.

To investigate interfacial electron transport during the HER, electrochemical impedance spectroscopy (EIS) was employed to analyse the charge transfer of each sample (Figure 3e). In contrast to the OER, the HER is a typical multi-electron reduction process, wherein the interfacial charge transfer resistance directly influences the reaction rate. The figure reveals that the intercepts of all curves on the real axis at elevated frequencies are very similar, suggesting that the ohmic resistance (including solution and electrode contact resistance) of each sample is fundamentally identical, hence eliminating the possibility of systematic errors. The disparity in the diameter of the semicircle in the low-frequency domain directly indicates the charge transfer resistance of the HER: the Co-WO₃@Mn₂WO₄-0.6-O_v sample has the smallest semicircle diameter, signifying its lowest interfacial charge transfer resistance and negligible kinetic resistance for proton adsorption and reduction activities. All other samples exhibit greater charge transfer resistances than Co-WO₃@Mn₂WO₄-0.6-O_v, indicating that electron transfer processes are impeded to differing extents. The overall trend aligns perfectly with the results from the LSV, Tafel, and Cdl tests. This outcome elucidates, from the standpoint of interfacial electron transfer, the source of the superior HER performance of Co-WO₃@Mn₂WO₄-0.6-O_v, demonstrating that Co doping and oxygen vacancy engineering effectively enhance the interfacial electron transport pathway of the catalyst and reduce the kinetic barrier of the reaction. The three-dimensional phase angle–frequency–potential graphs in Figure 3f elucidate the interfacial reaction characteristics of the HER process throughout the frequency and potential dimensions. All samples demonstrate a unimodal distribution in phase angle, signifying a predominant interfacial reaction step during the hydrogen evolution process (HER). Co-WO₃@Mn₂WO₄-0.6-O_v exhibits a greater peak phase angle and a more defined peak shape, indicating enhanced interfacial capacitive behaviour, more thorough double-layer charging, and increased active site utilisation. Conversely, the pure-phase WO₃@Mn₂WO₄ displays a diminished peak phase angle and an expanded peak shape, signifying pronounced interfacial resistive behaviour and increased charge transfer resistance. This outcome further substantiates that Co-WO₃@Mn₂WO₄-0.6-O_v exhibits enhanced interfacial electron transfer efficiency and HER kinetics.

This study performed multi-dimensional characterization of the samples to systematically elucidate the electrocatalytic performance of the oxygen evolution process (OER), with the results reported as follows. Figure 4a illustrates the linear sweep voltammetry (LSV) curves for the OER of various catalyst samples in 1 M KOH alkaline conditions. In the potential range of 1.3–1.9 V vs. RHE, the current density of all samples rises with the applied potential. In comparison, the Co-WO₃@Mn₂WO₄-0.6-O_v sample demonstrates the maximum current density throughout the full potential range, whereas the Co-WO₃@Mn₂WO₄-0.6 Sample has the lowest current density, suggesting that Co-WO₃@Mn₂WO₄-0.6-O_v demonstrates enhanced OER catalytic efficacy. Figure 4b delineates the respective potentials of each catalyst sample at current densities of 5, 10, and 15 mA cm^{−2} to provide a more intuitive quantification and comparison of their performance. The results indicate that under all three current density settings, Co-WO₃@Mn₂WO₄-0.6-O_v demonstrates the lowest overpotentials of 350.6, 408.6, and 440.6 mV, respectively, whereas Co-WO₃@Mn₂WO₄-0.6 exhibits the largest overpotential, attaining 567 mV at 15 mA cm^{−2}. The remaining samples have moderate values. This outcome aligns completely with the trend noted in the LSV curves, further substantiating that Co-WO₃@Mn₂WO₄-0.6-O_v demonstrates the superior OER catalytic activity throughout the series.

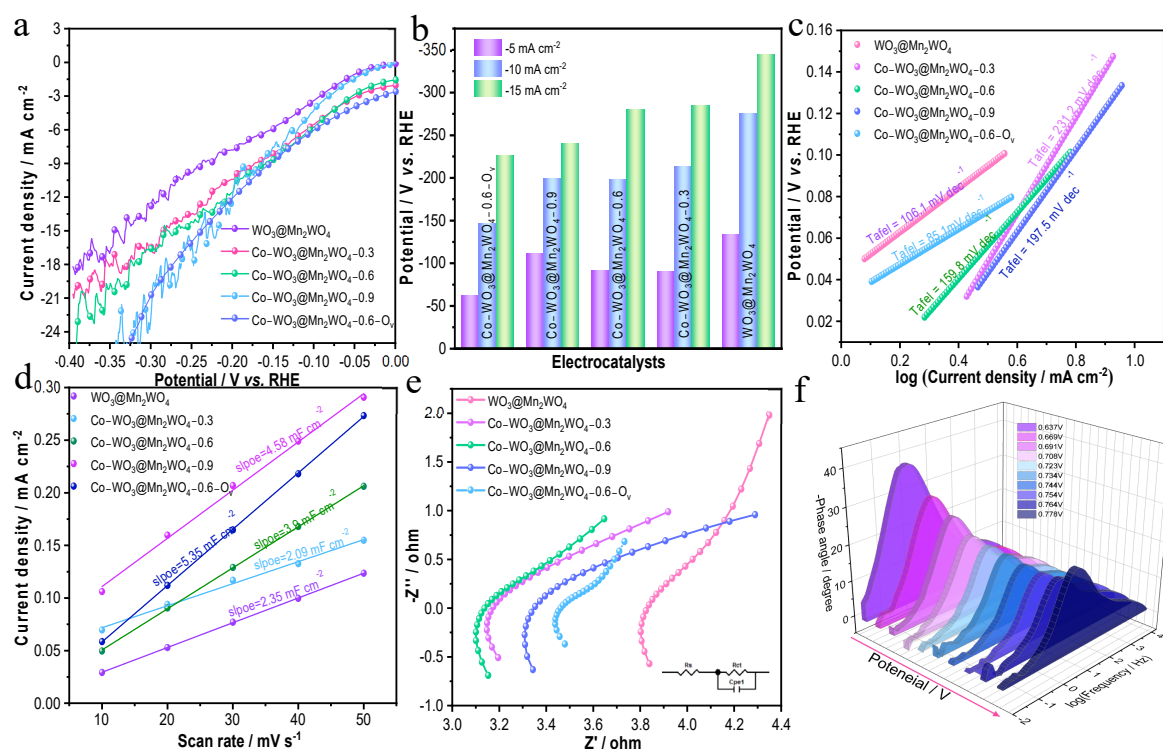


Figure 3. HER performance under alkaline media: (a) LSV curves; (b) overpotential comparison histogram; (c) Tafel slopes; (d) double-layer capacitance curves; (e) EIS plots; (f) 3D EIS plot.

The Tafel graphs (Figure 4c) elucidate the variations in reaction kinetics across the various catalysts. The Tafel slopes exhibit considerable variation among the samples: Co-WO₃@Mn₂WO₄-0.6-O_v exhibits the lowest Tafel slope of merely 65.0 mV dec⁻¹, the lowest recorded among all samples. Conversely, WO₃@Mn₂WO₄ and Co-WO₃@Mn₂WO₄-0.6 demonstrate Tafel slopes of 141.8 and 142.1 mV dec⁻¹, respectively. Among the other samples, Co-WO₃@Mn₂WO₄-0.9 (77.5 mV dec⁻¹) and Co-WO₃@Mn₂WO₄-0.3 (79.5 mV dec⁻¹) exhibit markedly lower slopes compared to the pure-phase sample. A reduced Tafel slope signifies a more rapid increase in current density with applied potential, indicating enhanced response kinetics. This outcome verifies that Co doping and subsequent treatments markedly enhance the OER kinetics of the catalysts, with Co-WO₃@Mn₂WO₄-0.6-O_v demonstrating the most rapid reaction kinetics.

The double-layer capacitance (Cdl) of each sample was determined (Figure 4d) to elucidate the fundamental structural factors contributing to performance enhancement, thereby assessing the electrochemically active surface area (ECSA) and the quantity of active sites. The Cdl value is derived from the slope of the linear fit of current density against scan rate; a steeper slope signifies a greater active surface area and an increased number of reaction sites. The results indicate that Co-WO₃@Mn₂WO₄-0.6-O_v has a slope of 0.05979 mF cm⁻², signifying the highest electrochemically active surface area, which provides more effective catalytic sites and offers an adequate reaction interface for OER. Conversely, Co-WO₃@Mn₂WO₄-0.6 and the pure-phase WO₃@Mn₂WO₄ demonstrate markedly reduced slopes, signifying a diminished number of active sites. This outcome, from the fundamental viewpoint of active site density, elucidates the underlying rationale for Co-WO₃@Mn₂WO₄-0.6-O_v demonstrating accelerated kinetics and enhanced catalytic activity. Subsequently, the electrochemical impedance spectroscopy (EIS) graphs (Figure 4e) provide a deeper analysis of the interfacial charge transfer kinetics. The curve characteristics reveal that the intercepts of all samples on the real axis are comparable, suggesting that the ohmic resistance (Rs) is fundamentally uniform across all samples, hence excluding the influence

of solution resistance and electrode contact resistance. Simultaneously, distinct variations in the semicircle diameters are evident: Co-WO₃@Mn₂WO₄-0.6-O_v exhibits the shortest semicircle diameter, signifying the lowest charge transfer resistance (R_{ct}) and the most rapid interfacial charge transfer; conversely, Co-WO₃@Mn₂WO₄-0.6 displays the largest semicircle diameter, the highest charge transfer resistance, and impeded interfacial reaction kinetics. The results indicate that Co doping and oxygen vacancy engineering significantly diminish interfacial charge transfer resistance and enhance electron transfer, supporting the findings from the Tafel kinetic study.

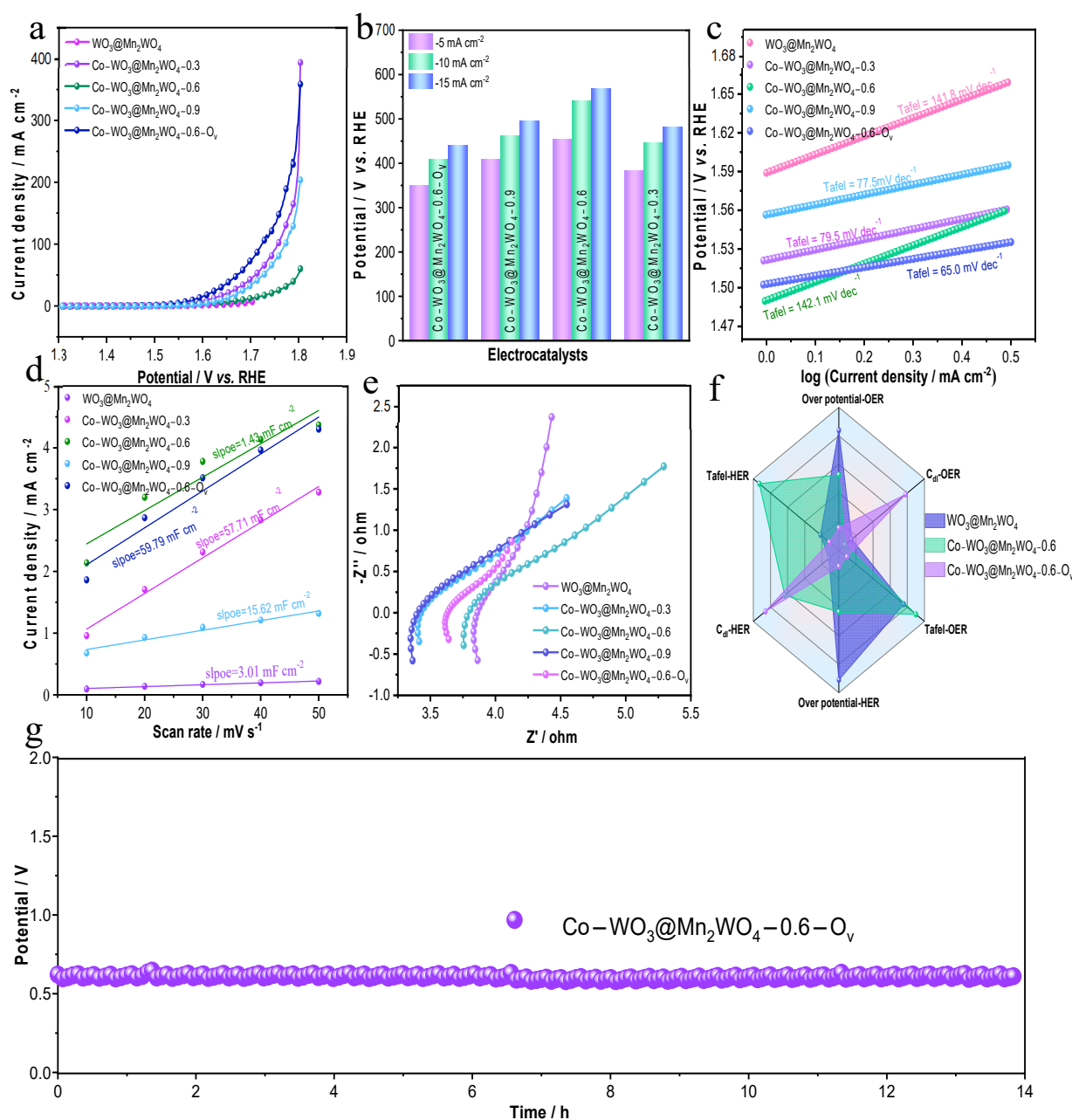


Figure 4. (a) OER LSV polarization curves; (b) overpotential histogram; (c) Tafel slope curves; (d) fitting curves of electrochemical double-layer capacitance (Cdl); (e) electrochemical impedance spectroscopy plots; (f) performance radar chart; (g) cyclic stability test.

Following the thorough characterisation of the OER single-function performance, the radar chart in Figure 4f offers a clear comparison of six essential performance indicators for OER and HER across three catalysts: WO₃@Mn₂WO₄, Co-WO₃@Mn₂WO₄-0.6, and Co-

$\text{WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.6\text{-O}_v$. The indicators comprise overpotential, double-layer capacitance, and Tafel slope. Regarding the OER-related parameters, $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.6\text{-O}_v$ demonstrates the lowest overpotential, the greatest Cdl value, and the smallest Tafel slope, aligning perfectly with the previous OER single-function characterisation. This sample exhibits the lowest overpotential and the highest Cdl value for HER-related metrics, demonstrating much superior catalytic activity and active site exposure compared to other samples, albeit marginally behind $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.6$ for HER Tafel slope. Upon evaluating all six metrics, $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.6\text{-O}_v$ exhibits significant benefits in both OER and HER major performance metrics, establishing it as the superior bifunctional electrocatalyst in this investigation.

Following the demonstration of the superior HER catalytic activity and kinetic properties of the $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.6\text{-O}_v$ sample, we further assessed its catalytic stability by prolonged chronopotentiometry, as illustrated in Figure 4g. The catalyst was cycled for 14 h at a constant current density. The graph indicates that the catalyst's working potential remained consistent during the test, exhibiting no substantial increase or fluctuation, so demonstrating that $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.6\text{-O}_v$ possesses exceptional electrochemical stability. In conjunction with the prior analysis of HER activity, overpotential, Tafel slope, Cdl, EIS, and the radar chart, this catalyst exhibits not only exceptional intrinsic activity and reaction kinetics but also remarkable long-term stability, thereby affirming its structural integrity and durability throughout the reaction. This outcome offers a significant assurance for its use in practical water electrolysis systems. Furthermore, to investigate the structural basis of the performance discrepancies, cyclic voltammetry (CV) curves were obtained at different scan rates (Figure S2). The present disparity in the non-Faradaic region has a linear relationship with the scan rate. The optimal sample demonstrates the greatest current disparity in the CV measurements, which corroborates the Cdl results presented in Figure 4d of the main text, signifying its extensive electrochemically active surface area and consequently offering numerous reaction sites to facilitate its superior alkaline HER/OER performance.

The acidic HER is crucial for practical applications; hence, we further assessed the HER performance of the catalysts in acidic environments. Figure 5a illustrates the linear sweep voltammetry (LSV) profiles of several catalysts in a 0.5 M H_2SO_4 acidic solution. $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.6\text{-O}_v$ has the maximum current density at the same applied potential, attaining around -400 mA cm^{-2} at -0.6 V vs. RHE , markedly surpassing the other samples. Conversely, pristine $\text{WO}_3@\text{Mn}_2\text{WO}_4$ has the most gradual rise in current density, reaching merely approximately -250 mA cm^{-2} at the same potential. The current densities of the other samples, specifically $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.3$, $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.6$, and $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.9$, are situated between these two extremes. The results clearly indicate that $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.6\text{-O}_v$ has the highest HER rate and inherent catalytic activity in acidic conditions. To further quantify and validate the variations in current density, the overpotentials at three current densities (-10 , -30 , and -50 mA cm^{-2}) were obtained from the LSV curves, and the findings are illustrated in Figure 5b. Among all samples, $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.6\text{-O}_v$ demonstrates the lowest overpotential throughout all samples at each of the three current densities, sustaining a low overpotential of 221 mV even at an elevated current density of -50 mA cm^{-2} .

This signifies its outstanding high-current-density catalytic efficacy in acidic environments, which aligns perfectly with the current density trend noted in the LSV curves. Subsequently, the Tafel plots in Figure 5c elucidate the reaction kinetics of acidic hydrogen evolution process (HER) for each sample. The results indicate substantial variations in the Tafel slopes across the samples. $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.6\text{-O}_v$ demonstrates the lowest Tafel slope of 53.8 mV dec^{-1} , succeeded by $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4\text{-}0.9$ at 74.6 mV dec^{-1} . Conversely,

pristine $\text{WO}_3/\text{Mn}_2\text{WO}_4$ exhibits a significantly elevated Tafel slope of $277.7 \text{ mV dec}^{-1}$, signifying sluggish kinetic processes. The findings indicate that Co doping and the engineering of oxygen vacancies efficiently enhance the adsorption-desorption equilibrium of hydrogen intermediates, substantially reducing the reaction's kinetic barrier. This outcome is strongly aligned with the LSV curve and overpotential analyses, offering direct kinetic proof for the superior acidic HER performance. To investigate the fundamental causes of the disparities in acidic HER performance, the electrochemically active surface area (ECSA) of each sample was assessed by double-layer capacitance (C_{dl}) measurements, as illustrated in Figure 5d. The C_{dl} value, indicated by the slope of the linear relationship between the current density difference and the scan rate at various scan rates, signifies the ECSA; a steeper slope denotes a greater ECSA and an increased number of active sites for the reaction. The fitting findings indicate substantial variations in C_{dl} values among the samples. $\text{Co-WO}_3/\text{Mn}_2\text{WO}_4-0.6-\text{O}_v$ demonstrates the maximum linear slope of 57.92 mF cm^{-2} , succeeded by $\text{Co-WO}_3/\text{Mn}_2\text{WO}_4-0.6$ at 51.85 mF cm^{-2} , whilst pristine $\text{WO}_3/\text{Mn}_2\text{WO}_4-0.9$ presents the lowest slope of 14.25 mF cm^{-2} , signifying the smallest C_{dl} value. The results, in terms of the quantity of active sites, elucidate the basic rationale for the enhanced acidic HER performance of $\text{Co-WO}_3/\text{Mn}_2\text{WO}_4-0.6-\text{O}_v$; greater ECSA facilitates more proton adsorption sites and reaction interfaces, hence enhancing proton adsorption and reduction in acidic conditions, which is supported by the LSV curve, overpotential comparison, and Tafel kinetic analysis.

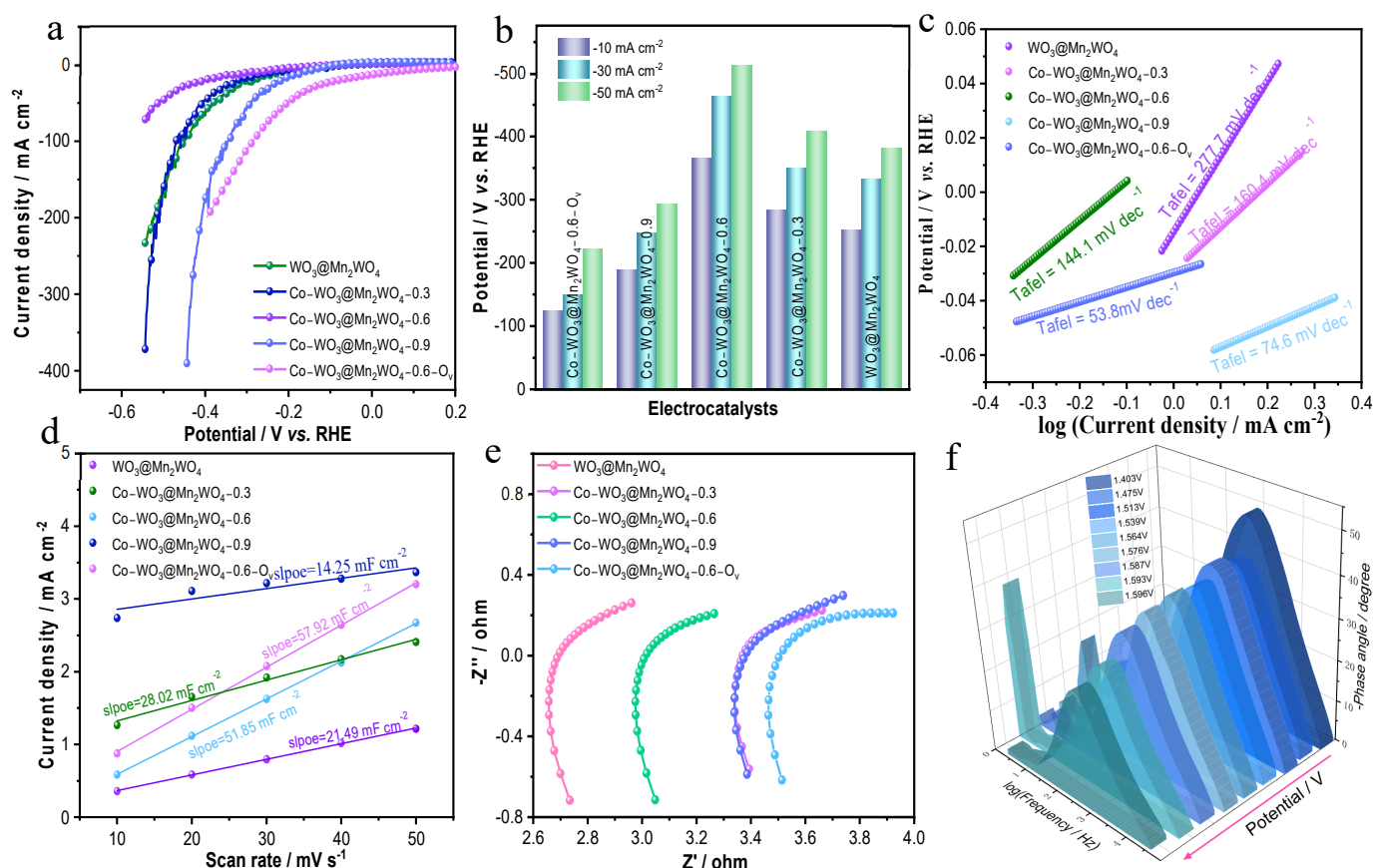


Figure 5. HER performance in acidic media: (a) LSV curves; (b) overpotential histogram; (c) Tafel slope plots; (d) double-layer capacitance curves; (e) EIS plots; (f) 3D EIS plot.

The evolution of the HER interfacial process with respect to potential and frequency was examined using three-dimensional Bode plots of phase angle against frequency and potential, as seen in Figure 5f. The position, height, and width of the phase angle peak

correspond to the reaction time constant, interfacial capacitance characteristics, and process homogeneity, respectively. All samples display a singular peak characteristic, signifying that the acidic HER is governed by a sole kinetic mechanism. With an increase in overpotential, the peak of the phase angle changes to elevated frequencies, and its amplitude intensifies. Co-WO₃@Mn₂WO₄-0.6-O_v demonstrates a more obvious and sharper phase angle peak, indicating enhanced interfacial capacitance behaviour, an optimised electron transfer channel, and more uniform reaction kinetics, which collectively corroborate the findings presented in Figure 5c,e. These findings unequivocally illustrate that Co doping and oxygen vacancy engineering collaboratively modulate the electronic structure and interfacial characteristics, markedly improving the electrocatalytic hydrogen evolution performance in acidic environments.

The catalysts' appropriateness for acidic water electrolysis was thoroughly assessed by methodically investigating their acidic OER performance, as seen in Figure 6. Figure 6a illustrates the OER polarisation curves of several catalysts in an acidic electrolyte. As the applied potential increases positively, the current density of all samples rises markedly, demonstrating characteristic acidic OER polarisation behaviour. At identical potentials, Co-WO₃@Mn₂WO₄-0.6-O_v demonstrates the largest current density, signifying the most rapid water oxidation rate in acidic conditions. Conversely, the current densities of the remaining Co-doped samples progressively rise with the optimisation of the Co doping ratio. These results clearly indicate that the synergistic integration of cobalt doping and oxygen vacancies markedly improves the intrinsic activity of the catalysts for acidic OER. To quantitatively assess the activity discrepancies noted in the polarisation curves, the overpotentials at current densities of 10, 30, and 50 mA cm⁻² were extracted from the LSV curves, as illustrated in Figure 6b. As the current density escalates, the overpotential of each sample correspondingly increases, aligning with the heightened kinetic resistance at elevated current densities in acidic oxygen evolution reactions. A study of various samples demonstrates that Co-WO₃@Mn₂WO₄-0.6-O_v displays the lowest overpotential across all current densities, signifying reduced energy consumption even at elevated reaction rates in acidic environments. Conversely, the pristine WO₃@Mn₂WO₄ sample constantly exhibits the largest overpotential, aligning perfectly with the patterns observed in the polarisation curve. Subsequently, the Tafel graphs in Figure 6c elucidate the reaction kinetics of acidic OER for each sample. The fitted findings indicate notable discrepancies in Tafel slopes across the samples. Co-WO₃@Mn₂WO₄-0.6-O_v possesses the lowest Tafel slope at 210.1 mV dec⁻¹, but pure WO₃@Mn₂WO₄ displays a significantly greater slope of 365.1 mV dec⁻¹, signifying sluggish kinetics. This indicates that Co doping and engineering of oxygen vacancies effectively enhance the adsorption desorption equilibrium of oxygen intermediates during acidic OER, substantially lowering the kinetic barrier. This data aligns well with the LSV and overpotential comparisons, offering direct kinetic evidence for the superior acidic OER performance.

The double-layer capacitance measurements depicted in Figure 6d reveal distinct variations in C_{dl} values across the samples. Co-WO₃@Mn₂WO₄-0.6-O_v has the greatest linear slope (0.00212 mF cm⁻²), signifying the most substantial electrochemically active surface area (ECSA) and the maximum quantity of available active sites. Conversely, the pure WO₃@Mn₂WO₄ and other samples display very low C_{dl} values, further indicating that a deficiency of active sites is a significant constraint on their performance. The superior acidic OER performance of Co-WO₃@Mn₂WO₄-0.6-O_v is attributable to the synergy of an increased number of active sites and enhanced intrinsic activity, as evidenced by the activity and kinetic findings. Electrochemical impedance spectroscopy was utilised to examine the interfacial charge transfer properties during the acidic OER, as illustrated in Figure 6e. The curves of all samples virtually converge at the origin of the real axis, signifying similar so-

lution ohmic resistances across the measurement systems and well regulated experimental conditions. The diameter of the semicircle in the impedance curve is directly correlated with charge transfer resistance; a reduced semicircle diameter signifies diminished interfacial charge transfer resistance and enhanced reaction kinetics. Analysis indicates that $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4-0.6-\text{O}_v$ exhibits the shortest semicircle diameter, markedly diminished charge transfer resistance, and enhanced electron migration and transfer efficiency at the catalyst/electrolyte interface. Conversely, the pure $\text{WO}_3@\text{Mn}_2\text{WO}_4$ demonstrates the most extensive capacitive arc diameter, significant charge transfer resistance, and sluggish interfacial kinetics. The results validate the LSV and Tafel investigations, thoroughly elucidating the superior acidic OER catalytic benefits of the improved catalyst from an interfacial impedance standpoint.

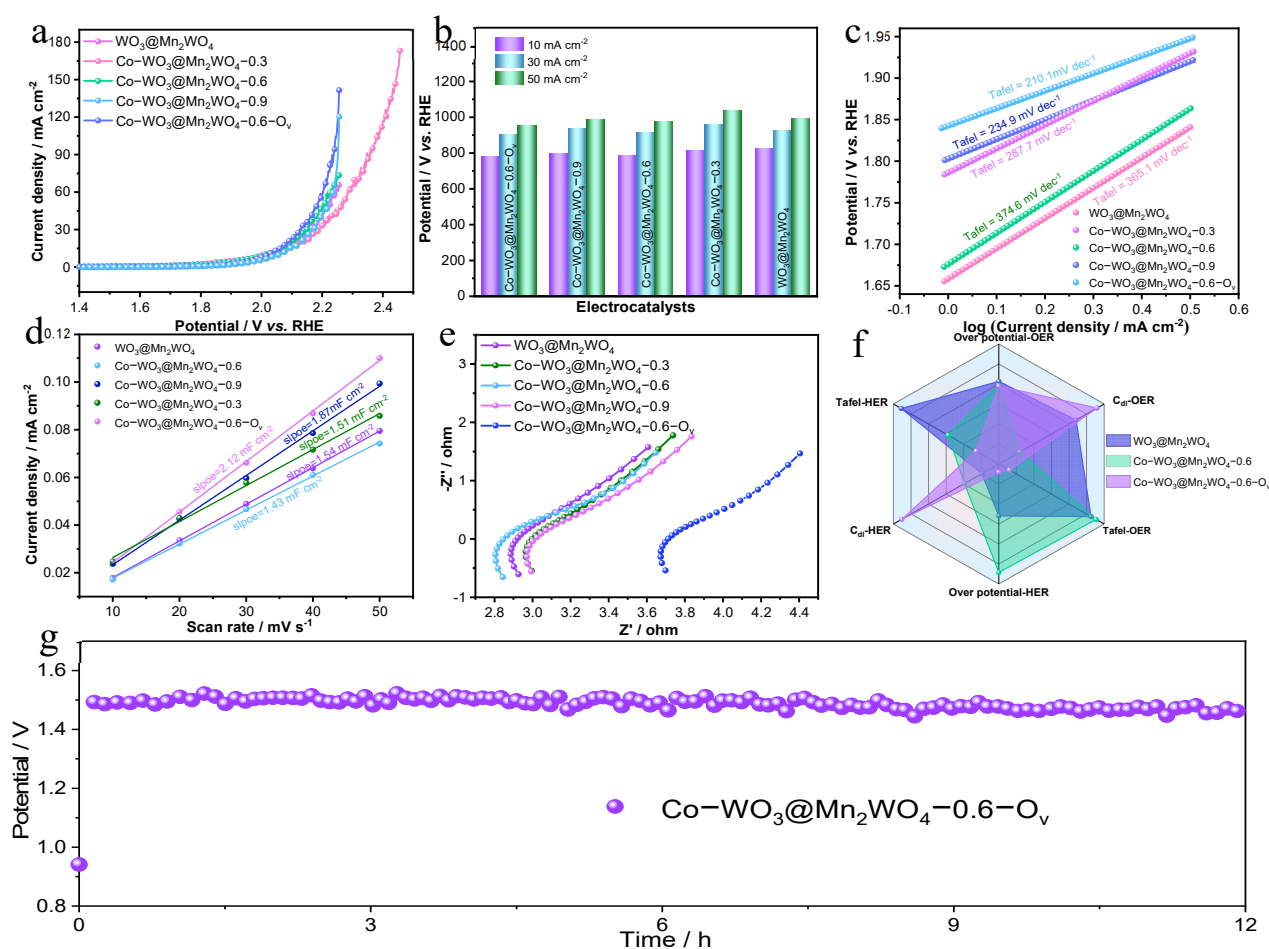


Figure 6. OER performance in acidic media: (a) LSV curves; (b) overpotential histogram; (c) Tafel slopes; (d) double-layer capacitance curves; (e) EIS plots; (f) performance radar chart; (g) cyclic stability test.

A three-dimensional radar map was employed to thoroughly assess the acidic OER performance of the catalysts by comparing three critical parameters: overpotential, Tafel slope, and Cdl (Figure 6f). The findings indicate that for the OER half-reaction, $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4-0.6-\text{O}_v$ is positioned innermost on both the Overpotential-OER and Tafel-OER axes, while being outermost on the Cdl-OER axis. This indicates that it exhibits the lowest overpotential, the fastest reaction kinetics, and the largest electrochemically active surface area, resulting in superior OER performance compared to the other two catalysts. The same applies to the HER half-reaction. $\text{Co-WO}_3@\text{Mn}_2\text{WO}_4-0.6-\text{O}_v$ is the sole sample that demonstrates superior performance across all critical metrics for both the

HER and OER half-reactions, showcasing its effective bifunctional catalytic capability for hydrogen and oxygen evolution in acidic media, thereby establishing it as the catalyst with the highest overall performance in this series. To initially evaluate the catalyst's stability in acidic conditions, chronopotentiometry testing was conducted on the ideal sample Co-WO₃@Mn₂WO₄-0.6-O_v for a duration of 12 h. Figure 6g illustrates that, with a constant current density, the catalyst's operating potential remains relatively stable throughout the testing period, signifying robust operational stability and corrosion resistance during acidic OER.

The CV curves at various scan rates within the acidic OER system depicted in Figure S3 constitute the foundational data for the Cdl fitting outcomes presented in Figure 6d of the main article. The trend of the current difference relative to the scan rate aligns with the Cdl values, further confirming that Co-WO₃@Mn₂WO₄-0.6-O_v has a greater electrochemically active surface area. To enhance the validation of the catalyst's performance and stability under actual settings, membrane electrode tests, polarisation curves for both acidic and alkaline total water splitting, and a 40-h long-term cycle stability test were conducted (Figure S4). The findings indicate that the optimal sample displays a stable temperature response and interfacial charge transfer properties within the membrane electrode setting, exhibits superior catalytic activity in both acidic and alkaline overall water splitting systems, and experiences no substantial potential fluctuations during the 40-h cycling test, thereby affirming its applicability and long-term stability in practical water electrolysis devices.

4. Conclusions

In this work, we successfully fabricated a Co-doped WO₃@Mn₂WO₄ core shell heterostructure with controllably engineered surface oxygen vacancies via a facile two-step hydrothermal-reduction route. The optimized Co-WO₃@Mn₂WO₄-0.6-O_v sample delivers outstanding bifunctional HER and OER catalytic activity across both acidic and alkaline electrolytes, featuring low overpotentials, small Tafel slopes, enlarged electrochemical active surface area (high Cdl), and accelerated interfacial charge transfer kinetics. When integrated into a membrane electrode assembly for overall water splitting, the catalyst maintains robust electrocatalytic stability for over 40 h without obvious performance decay. Such remarkable catalytic advantages stem from the triple synergistic effect of Co heteroatom doping, abundant oxygen vacancy defects, and tightly bonded core shell interfaces. This research offers a reliable synergistic modification strategy and clear structure-activity insights to guide the rational construction of high-performance tungsten-based water-splitting electrocatalysts.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics14080208/s1>, Figure S1: Pie charts showing atomic percentage of elements in two catalyst samples; Figure S2: Cyclic voltammetry curves of various catalysts measured at scan rates ranging from 10 to 50 mV s⁻¹ under alkaline conditions; Figure S3: Cyclic voltammetry curves of various catalysts measured at scan rates ranging from 10 to 50 mV s⁻¹ under acidic conditions; Figure S4: Membrane electrode comparison; Table S1: HER performances of Co-WO₃@Mn₂WO₄-0.6-O_v with other W-based electrocatalysts; Table S2: OER performances of Co-WO₃@Mn₂WO₄-0.6-O_v with other W-based electrocatalysts.

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