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# Reversible oxygen vacancies in tungsten oxide-activated heterocatalysts enable stable electrocatalytic oxygen evolution

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## ABSTRACT

Interfacial and oxygen vacancy engineering are promising strategies to tune the electronic structure of electrocatalysts and modulate the surface absorption/desorption of reactants, thereby enhancing oxygen evolution reaction (OER) activity and stability. Herein, we present a hierarchical assembly strategy to mitigate Co dissolution and stabilize oxygen vacancies triggered by strong electronic interactions via constructing elaborately  $W_{18}O_{49}/Co_3(BO_3)_2$  heterostructure. Multiple in-situ characterization technologies confirm that this synergy enables the formation of active centers and accelerates charge transfer, resulting in improved oxygen evolution activity. Importantly, the incorporation of  $W_{18}O_{49}$  provides dynamically reversible oxygen vacancies that enhance catalysis durability, stabilizing the active Co sites during OER processes. Theoretical calculations further reveal that the interfacial electronic interaction enhances charge transfer, suppresses cobalt ions demetalization, and stabilizes oxygen vacancy within the crystal structure. Owing to the stabilized Co sites and O sites, the  $W_{18}O_{49}/Co_3(BO_3)_2$  exhibits high activity (251 mV at 10 mA cm<sup>-2</sup>) and outstanding stability, with minimal degradation after 100 hours of operation. This work offers valuable insights into designing highly active and durable OER catalysts by leveraging heterointerfacial and oxygen vacancy engineering.

#### 1. Introduction

Hydrogen, with high gravimetric energy density, is an ideal replacement for traditional fossil fuels and also a pivotal ingredient in essential industrial chemicals [1]. Water electrolysis powered by renewable electricity offers great promises for eco-friendly green hydrogen energy production [2–4]. The oxygen evolution reaction (OER), a crucial half-reaction of electrochemical water splitting, is hindered by slow multi-step proton-coupled processes, and efficient catalysts for OER still primarily rely on precious metals [5,6]. Presently, Ruthenium (Ru) and Iridium (Ir) metals-based materials are still considered to be state-of-the-art OER electrocatalysts, nevertheless, the high cost and scarcity in crust hampers the application in industry [7,8].

To enable the practical electrolytic water-splitting system, nonprecious electrocatalysts with high activity and stability are considered to be found to reduce energy consumption [9,10]. Consequently, there has been a shift towards exploring earth-abundant transition metal-based electrocatalysts, particularly transition metal oxides, phosphide, and borate, known for their structural stability and versatile electronic structures [11–14]. However, the catalytic activity and stability of transition metal materials have yet to satisfy the requirements of practical applications and therefore require further enhancement.

Essentially, the OER activity of an electrocatalyst is highly dependent on both the quantity and the intrinsic activity of its active sites. To this end, various modification strategies, involving morphological control [15], heterostructure construction [16], and defect engineering [17],

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have been employed to enhance catalytic performance. Among them, the interfacial electronic effects between different components exert incredible control over the activation of the active site. For instance, the interface "sp C-O-Mo hybridization" in graphdiyne/molybdenum oxide (GDY/MoO<sub>3</sub>) activated new intrinsic catalytic active sites with exponential multiplication [18]. Fundamentally, the core of catalytic enhancement driven by interfacial interaction lies in affecting the dynamic behavior of the reactive adsorbed species at the active sites [19]. Du et al. proposed a highly active Ru/Co dual atom active site that can be generated around the RuO<sub>2</sub>/CoO<sub>x</sub> interface to synergistically adsorb the oxygen intermediates, leading to a favourable reaction path [20]. Beyond the interfacial effect, the defect is a potent tool for refining the electrocatalytic competencies. Oxygen vacancies (Ov) engineering, playing a significant role in altering the coordination environment of the metal active center, exposing more active sites, and enhancing the intrinsic catalytic activity, can be created by hydrogen reduction, high temperature calcination, or doping with low-valent element [21,22]. Mefford et al. showed that the increase of Sr dopants in  $La_{1-x}Sr_xCoO_{3-\delta}$ led to higher O<sub>v</sub>, greater covalency of the Co-O bond, and better OER activity [23]. Wang's group revealed that an unusual vacancy induction in typical Co<sub>3</sub>O<sub>4</sub> facilitated the intermediates Co-OOH deprotonation process at a lower potential, thus promoting OER performance [24]. Despite these successful examples, untunable O<sub>v</sub> can lead to unfortunate activity and stability. As per the previous report, the O<sub>v</sub> is barely reversible in PrSr<sub>3</sub>Co<sub>1.5</sub>Fe<sub>1.5</sub>O<sub>10</sub>/SrCoO<sub>3-x</sub> easily deteriorates the intrinsic activity and crystal structure stability [25]. Reversible O<sub>v</sub> ensures the coordination environment of the metal active sites even after repeated electrochemical reactions. Therefore, chemically stable O<sub>v</sub> and active centers are crucial for complementarily enhancing good activity and maintaining the dynamically steady surface of catalysts. Comfortably, Lv et al. reported the strong interaction between Ru and TiO<sub>x</sub> in Ru/TiO<sub>x</sub>, which facilitates dynamic O<sub>v</sub> regeneration and contributes to being highly active and stable [26]. The construction of heterojunctions is expected to introduce reversible O<sub>v</sub>, but there are fewer reports on it, and the exact mechanism remains unclear.

In recent studies, oxygen-defective tungsten oxides have been discovered to have great potential in electrocatalysis. However, research on tungsten-based OER catalysts still remains limited. Tungsten oxides with high valence states are generally unstable in alkaline conditions. However, they still participate in water splitting due to favorable thermodynamics for oxygen evolution at high pH. Notably, tungsten oxides with mixed valence states (V and VI) demonstrate stable OER activity. Earth-abundant tungsten oxides (WO3-x), especially monoclinic and non-stoichiometric W18O49 have attracted great interest owing to its high chemical stability and large number of O<sub>v</sub> [27]. The O<sub>v</sub> are easily generated around the tri-coordinated oxygen atoms located at the edges of the octahedral units within the crystal structure, facilitate the adsorption/desorption of \*OH and \*OOH intermediates during the OER process [28]. Therefore, W<sub>18</sub>O<sub>49</sub> exhibit a more robust structure and enhanced stability in alkaline solutions, suggesting that partial reduction of tungsten can improve the stability of its oxides for OER applications [29]. Meanwhile, self-supporting tungsten oxide material is considered a favorable conductive material, that facilitates electron transfer and the formation of heterogeneous interfaces. According to literature, metal borates have attracted tremendous attention in the field of electrocatalysis in recent years, owing to the ability of boron to supply more electron-rich metal centers for catalysis [30]. Nevertheless, the catalysts based on metal borate still face some disadvantages such as boron leaching from the catalyst during operation and lack of versatility in effectively catalyzing all aspects related to overall water splitting [31]. Taken together, it is ideal to combine the advantages of both oxygen vacancy and interfacial engineering to achieve the construction of reversible O<sub>v</sub> and stable active centers in the transition metal borate doped self-supporting tungsten oxide material, thereby enhancing its catalytic performance.

In this work, we report an innovative system featuring oxygen-

deficient Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> ultrathin nanosheets anchored on tungsten oxide nanowires (W18O49/Co3(BO3)2). A comprehensive suite of operando characterizations has been employed to track the potential-dependent dynamic response of the interface and O<sub>v</sub> during the OER. We elucidate the mechanism by which reversible O<sub>v</sub> derived from heterojunctions enhance intrinsic activity and stability under dynamic conditions. The in-situ Raman spectroscopy and in-situ electrochemical impedance spectroscopy (EIS) demonstrate the efficacy of synergistic effects between W18O49 and Co3(BO3)2 in promoting the formation of CoOOH active center and charge transfer to improve oxygen evolution activity. Beyond the significant enhancement in catalytic activity, the incorporation of the W<sub>18</sub>O<sub>49</sub> substrate provides reversible O<sub>v</sub> for durable catalysis, which stabilizes the active Co sites during the OER process, as proven by in-situ X-ray photoelectron spectroscopy (XPS). Impressively, the optimized W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> exhibits remarkable OER performance with an overpotential of 251 mV at a current density of  $10 \text{ mA cm}^{-2}$ , and long-durable stability of 100 h, suppressing most active OER electrocatalysts. Density functional theory (DFT) further confirmed that the regulation mechanism of the interface, which improves the ratedetermining steps by optimizing the adsorption/desorption behavior of intermediates, thereby significantly enhancing the oxygen evolution kinetics.

## 2. Results and discussions

The synthesis process of the self-supported  $W_{18}O_{49}/Co_3(BO_3)_2$  electrode is schematically shown in Fig. 1a. Through a facile hydrothermal and soaking process, porous W<sub>18</sub>O<sub>49</sub> nanowire clusters are in-situ grown on Ni foam (NF), followed by the straightforward anchoring of Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> (cobalt borate) nanosheets via a sodium borohydride (NaBH<sub>4</sub>) reduction method. Specifically, the dark navy blue W<sub>18</sub>O<sub>49</sub> nanowire clusters were initially grown in situ on NF by hydrothermal treatment of WCl6 ethanol solution. W18O49 not only serves as an appropriate component but also a suitable substrate, laying the foundation for enhancing the overall electrical activity, conductivity, and stability. Subsequently, the  $W_{18}O_{49}$  was immersed in the NaBH<sub>4</sub> solution containing Co(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O, resulting in black W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> composites. This approach features the entangled growth of  $Co_3(BO_3)_2$ nanosheets on W18O49 nanowires, providing a structural foundation for strong interfacial geometric and electronic interaction between Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> and W<sub>18</sub>O<sub>49</sub> substrate. Crystal and compositions of W<sub>18</sub>O<sub>49</sub>/ Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> composites were investigated by X-ray diffraction (XRD) measurements, which were scraped off from NF. As depicted in Fig. 1b, the diffraction peaks in the XRD pattern can well correspond to orthorhombic Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> (JCPDS 25-0102) and monoclinic W<sub>18</sub>O<sub>49</sub> (JCPDS 05-0392), preliminarily confirming the successful preparation of heterostructure. Moreover, the XRD Rietveld refinement method is applied to verify the crystal structure of  $W_{18}O_{49}$  and  $Co_3(BO_3)_2$  in Fig. S1a. The fitting parameters in Table S1 and calculated patterns indicate acceptable correlation between observed and calculated XRD patterns. For comparison, bare  $W_{18}O_{49}$  and  $Co_3(BO_3)_2$  compounds with pure single phases were also prepared, as validated by corresponding XRD (Fig. S1bc). Raman spectroscopy was used to further confirm the structural information on the as-synthesized catalysts. The Raman peaks at around 194, 485, and 690 cm<sup>-1</sup> corresponding to the F<sup>1</sup><sub>2 g</sub>, E<sub>2 g</sub>, and A<sub>1 g</sub> phonon modes severally [32], which are attributed to the tensile vibration of Co-O in hierarchical structured W18O49/Co3(BO3)2. It is noteworthy that the characteristic peaks of W-O are not detected due to the anchoring of Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> nanosheets during the second step. Apparently, it could be observed that the Raman peak intensity of the composite exceeds that of simplex Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, signifying that more pronounced Co-O bonds and stronger electronic interaction in the composite (Fig. S3). In addition, we also analyzed the XRD and Raman spectra of  $W_{18}O_{49}/Co_3(BO_3)_2$  heterostructure formed by different amounts of Co(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O, indicating that the quantity of cobalt has no effect on the crystal structure (Fig. S4). Evidently, gas adsorption investigations confirm the typical existence of



**Fig. 1.** Catalyst design and structured characterization. (a) Schematic illustration of the preparation process, (b) XRD pattern, (c) SEM and (d) TEM images of  $W_{18}O_{49}/Co_3(BO_3)_2$ . (e) AFM image and the corresponding height profiles. (f) High-resolution TEM image and (g) the corresponding IFFT images and atomic structure of  $W_{18}O_{49}$  and  $Co_3(BO_3)_2$  in  $W_{18}O_{49}/Co_3(BO_3)_2$ , respectively. (h) The HAADF-STEM image and corresponding EDS mapping images of  $W_{18}O_{49}/Co_3(BO_3)_2$ .

mesopores in the as-synthesized hybrid (Fig. S5). Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) images of as-synthesized catalysts show that the W<sub>18</sub>O<sub>49</sub> nanowire clusters recombined uniformly with Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> nanosheets (an average thickness of  $\sim 1.5$  nm) (Fig. 1a-e and Fig. S6). Such ultrathin nanosheets allow more atoms to be exposed, providing effective active sites for catalytic reactions. The in-situ formed W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> heterostructure is supported by the W<sub>18</sub>O<sub>49</sub> substrate, which prevents agglomeration of the Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> nanosheets in addition to stabilizing the structure. Noticeably, the above easily reducible NaBH4 method typically leads to low crystallinity [33]. In the high-resolution TEM (HR-TEM) image, the hypocrystalline region at the bottom right is connected to the crystalline region at the top left, corresponding to Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> and W<sub>18</sub>O<sub>49</sub>, respectively (Fig. 1f and Fig. S7a). The corresponding inverse fast Fourier transform (IFFT) and the schematic diagram of atomic structure show the lattice fringes of 0.378 and 0.269 nm well match with the (010) and (121) crystal planes of  $W_{18}O_{49}$ and Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, respectively (Fig. 1g and Fig. S8). Meanwhile, the representative selected area electron diffraction (SAED) in Fig. S7b

confirms the existence of lattice facets of  $W_{18}O_{49}$  (010) and  $Co_3(BO_3)_2$  (121). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the corresponding energy dispersive spectrometer (EDS) images of  $W_{18}O_{49}/Co_3(BO_3)_2$  demonstrate the homogeneous distribution of Co, W, B, and O signals throughout the entire heterostructure (Fig. 1h and Fig. S9). The inductively coupled plasma mass spectrometry (ICP-MS) test reveals that the  $W_{18}O_{49}/Co_3(BO_3)_2$  comprises Co (66.26 %/2.98 mg cm<sup>-2</sup>) and W (8.12 %/0.36 mg cm<sup>-2</sup>) (Table S2). The above results demonstrate the successful synthesis of the  $W_{18}O_{49}/Co_3(BO_3)_2$  composite structure with a well-defined supported  $W_{18}O_{49}$  under in situ conditions.

Electron paramagnetic resonance (EPR), as strong evidence for characterizing unpaired electrons, is used to explore the generation and variation of oxygen vacancies (O<sub>V</sub>). As depicted in Fig. 2a and Fig. S10, in comparison to both of the single-phase components, constructing a heterostructure based on  $W_{18}O_{49}$  and  $Co_3(BO_3)_2$  led to a noticeable increment in  $O_V$  (g=2.003) [34]. The increased O vacancies can be attributed to the electron transfer induced by interfacial interactions. X-ray photoelectron spectroscopy (XPS) was further utilized to

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**Fig. 2.** Electron and coordination structure characterization. (a) EPR spectra. XPS fine spectra in (b) Co 2p and (c) W 4 f region of  $W_{18}O_{49}/Co_3(BO_3)_2$ ,  $W_{18}O_{49}$ , and  $Co_3(BO_3)_2$ . (d) Normalized Co K-edge XANES of  $W_{18}O_{49}/Co_3(BO_3)_2$ ,  $Co_3(BO_3)_2$ ,  $Co_3(BO_3)_2$ , Co foil, CoO, and LaCoO<sub>3</sub>. (e) The corresponding Fourier transformed  $k^3$ -weighted EXAFS spectra and (f) Wavelet transform of  $k^3$ -weighted EXAFS signals. (g) Normalized W L<sub>3</sub>-edge XANES of  $W_{18}O_{49}/Co_3(BO_3)_2$ ,  $W_{18}O_{49}$ , W foil, WO<sub>2</sub>, and WO<sub>3</sub>. (h) The corresponding Fourier transformed  $k^3$ -weighted EXAFS spectra.

scrutinize the electronic structures of as-prepared materials. The Co 2p XPS spectra illustrate two strong peaks are assigned to Co 2p<sub>3/2</sub> and Co  $2p_{1/2}$  orbitals, along with satellite peaks (noted as Sat.) (Fig. 2b). Albeit no obvious difference in fitted peaks of W18O49/Co3(BO3)2 and  $Co_3(BO_3)_2$ , an increased ratio of  $Co^{2+}/Co^{3+}$  in  $W_{18}O_{49}/Co_3(BO_3)_2$  declares the existence of more oxygen vacancies after heterojunction formation[35]. For the W 4 f spectra, characteristic peaks are attributed to W 4  $f_{7/2}$ , W 4  $f_{5/2}$  orbitals as well as WO<sub>3</sub> loss feature peak (Fig. 2c) [36]. The ratio of  $W^{5+}$  species in the  $W_{18}O_{49}/Co_3(BO_3)_2$  was higher than that of pristine  $W_{18}O_{49}$  (Fig. S12a). This is likely due to the reduction effect during the NaBH4 treatment and the coupling effect, resulting in a higher degree of reduction of  $W^{6+}$  [37]. The O 1 s XPS to verify the defective structure are shown in Fig. S11a. It can be seen that three well-fitted peaks are well deconvoluted into the lattice oxygen (OL) at 530.5 eV, O<sub>V</sub> at 531.4 eV, and adsorbed water (H<sub>2</sub>O<sub>ads</sub>) at 532.8 eV, severally [38,39]. In particular, the oxygen vacancies concentration in W18O49, Co3(BO3)2, and W18O49/Co3(BO3)2 shows an increasing trend due to the chemical environment change of O<sub>V</sub> caused by the interface effect, being consistent with the EPR results (Fig. S12b). Such notable variation in the proportion of  $O_V$  is observed from 35.6 % to 41.1 %,

demonstrating the abundance of  $O_V$  and the excellent electronic capture and transfer properties in the  $W_{18}O_{49}/Co_3(BO_3)_2$  hybrid catalyst. In Fig. S11b, the characteristic peak of B 1 s around 192.2 eV is assigned to B-O of borate.

The electronic structure and local coordination environment of assynthesized catalysts were further investigated by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements. The Co K-edge spectrum (Fig. 2d) exhibits the energy position of both  $W_{18}O_{49}/Co_3(BO_3)_2$  and  $Co_3(BO_3)_2$ samples lies between CoO and LaCoO3 references, visualizing the average valence state of Co is between + 2 and + 3, in line with the XPS results. Notably, the absorption edge for W18O49/Co3(BO3)2 shifts noticeably toward the lower energy relative to that of  $Co_3(BO_3)_2$ , implying the lower average Co valence state. In the meanwhile, the higher intensity of the white line for W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> compared with  $Co_3(BO_3)_2$  indicates more unoccupied p orbital due to the change in the local coordination environment. From the Co K-edge Fourier transforms EXAFS (FT-EXAFS) spectrum in Fig. 2e, the dominant peaks of W18O49/ Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> are attributed to the scattering of Co-O in the first shell and Co-Co in the second shell [40]. Besides, the peak intensity corresponding to the first shell of the  $W_{18}O_{49}/Co_3(BO_3)_2$  is lower, indicating a decrease in the number of coordinated oxygen [41]. Notably, W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> possesses prolonged Co-Co bond length with respect to Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, which may be due to lattice expansion in the homojunction at the interface. These results are also confirmed in the wavelet transform (WT) of Co K-edge FT-EXAFS in Fig. 2f. The coordination configuration and interatomic distances were further determined by quantitative least-squares EXAFS curve fitting analysis using Co-O scattering path. Compared with Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, the lower Co-O coordination number (CN) of W18O49/Co3(BO3)2 confirms the existence of more oxygen vacancies and a higher degree of disorder, in line with O 1 s XPS spectra results (Fig. S13 and Table S3) [19,42]. For the W L<sub>3</sub>-edge spectrum in Fig. 2g, the white line peak position of W18O49/Co3(BO3)2 falls between those of  $WO_2(+4)$  and  $WO_3(+6)$ , and its oxidation state is lower than that of the pristine W<sub>18</sub>O<sub>49</sub> due to the formation of increased oxygen vacancies. As shown in Fig. 2h, although the peak positions of the FT-EXAFS spectrum at the W L<sub>3</sub>-edge are almost identical, the intensity of W-O decreases in W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, indicative of a lower CN of W-O coordination, as a result of  $O_V$  [43]. Additionally, the WT-EXAFS analyses offer a higher resolution in the radial distance, further corroborating the EXAFS results (Fig. S14).

The electrochemical activity and stability of the as-prepared

catalysts in 1.0 M KOH were examined. As shown in Fig. S15, the redox peaks of the curves correspond to the redox reactions of Co. Typically, there are two pairs of redox peaks in both samples, which are attributed to  $Co^{II/III}$  and  $Co^{III/IV}$  [44]. The  $W_{18}O_{49}/Co_3(BO_3)_2$  shows more prominent Co<sup>III/IV</sup> redox peaks and a reduced overpotential for OER. Moreover, enhanced redox peaks and larger integrated areas indicate an increase in the number of electroactive sites. As can be seen from the iR-corrected linear sweep voltammetry (LSV) curves in Fig. 3a and Fig. S16. W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> exhibits significantly improved OER activity, with an overpotential of 251 mV at the current density of 10 mA cm<sup>-2</sup>, which is comparable to benchmark RuO<sub>2</sub> (210 mV) and notably lower than that of Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> (267 mV), W<sub>18</sub>O<sub>49</sub> (292 mV), and NF (411 mV). Moreover, W18O49/Co3(BO3)2 only requires overpotentials of 323 and 360 mV at 100 and 200 mA  $\rm cm^{-2}$ , demonstrating a much higher activity than those control catalysts (Fig. 3b). It is evident that the interfacial interaction directly affects the catalytic activity. Further insights into the kinetic mechanism are gleaned from the Tafel plot [45]. W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> exhibits the lowest Tafel slope of 58.9 mV dec<sup>-1</sup>, indicating the highest charge transfer efficiency and fastest reaction rate among these prepared samples (Fig. 3c). The electrochemical impedance spectroscopy (EIS) measurements also corroborate a faster OER process of W18O49/Co3(BO3)2, as evidenced by its remarkably



**Fig. 3.** Electrocatalytic OER performance. (a) LSV polarization curves of  $W_{18}O_{49}/Co_3(BO_3)_2$ ,  $W_{18}O_{49}$ ,  $Co_3(BO_3)_2$ ,  $RuO_2$ , and NF. (b) Overpotentials at 10, 100, and 200 mA cm<sup>-2</sup>. (c) Tafel plots derived from (a). Bode phase plots of (d)  $W_{18}O_{49}/Co_3(BO_3)_2$  and (e)  $Co_3(BO_3)_2$ . (f) Response of the phase angle to the applied potential for different catalysts. (g) Comparison with the reported literature. (h) Chronopotentiometric curve of  $W_{18}O_{49}/Co_3(BO_3)_2$  and  $Co_3(BO_3)_2$  at 10 mA cm<sup>-2</sup> (insets display the polarization curves of  $W_{18}O_{49}/Co_3(BO_3)_2$  before and after 5000 CV cycles).

lower charge transfer resistance ( $R_{ct}$ ) 1.5  $\Omega$  than that of other control samples (Fig. S17). In-situ EIS at different applied voltages was further employed to probe the electrocatalytic kinetics and the properties of the electrode/electrolyte interface during the OER process. The Nyquist plots revealed a faster decrease in the semicircle of W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> as a function of potential, indicating a faster charge transfer rate, as depicted in Fig. S18. Furthermore, in the EIS-derived Bode phase plots, the peak in the high-frequency region  $(10^2 - 10^5 \text{ Hz})$  is associated with intrinsic electron conduction of the electrocatalyst, whereas the peak in the low-frequency region  $(10^{-2} - 10^{1} \text{ Hz})$  is related to the charge transfer at the electrolyte-catalyst interface [46]. With the increased applied potentials, the phase angles at low frequency for W18O49/Co3(BO3)2 show an accelerating trend of decline than that of Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> and W<sub>18</sub>O<sub>49</sub>, indicating that the combination of Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> with W18O49 substrate can accelerate the electron transfer at electrolyte-catalyst interface and consequently lead to a superior OER kinetics (Fig. 3d-e and Fig. S19). From the above electrochemical results, it is clear that the synergic effect between W18O49 nanowires and Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> nanosheets, accompanied by increased oxygen vacancies, plays an important role in reducing charge-transfer resistance at the interfaces and ameliorating conductivity [47,48]. Additionally, the electrochemical double-layer capacitance (Cdl) values, extracted from cyclic voltammetry (CV, Fig. S20), are closely associated with the electrochemically active surface areas (ECSA) of the catalyst. W18O49/Co3(BO3)2 displays noticeably the highest Cdl and ECSA value  $(252.9 \text{ mF cm}^{-2}, 4215 \text{ cm}^2)$  with respect to its counterparts, suggesting the more surface-exposed active sites (Fig. S21 and S22a). In order to exclude the influence of different mass loadings, the LSV curves are normalized by ECSA to compare their intrinsic activity. As showcased in Fig. S22b, the ECSA-normalized current of W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> is distinctly higher than others, emanating excellent OER intrinsic activity. To quantitatively evaluate the mass activity, we determined the corresponding mass loading of the  $W_{18}O_{49}/Co_3(BO_3)_2$  and other control samples by ICP-MS measurement. The W18O49/CO3(BO3)2 exhibits the greatest mass activity of 0.06 A  $mg_{Co}^{-1}$  at an overpotential of 300 mV (Fig. S23a). The turnover frequency (TOF) values, corresponding to the intrinsic activity of the Co sites, also demonstrates the best performance of W18O49/Co3(BO3)2, with the TOF value of 0.003  $s^{-1}$  at  $\eta{=}$  300 mV, much higher than that of  $Co_3(BO_3)_2$  (0.00068 s<sup>-1</sup>) (Fig. S23b). Visibly, the  $W_{18}O_{49}/Co_3(BO_3)_2$  electrocatalyst outperforms to the comparison catalysts in terms of overpotential, Tafel slope, EIS, and Cdl, further proving the advantage of the self-supporting electrodes with hierarchical structures and interconnected conductive networks. Impressively, W18O49/Co3(BO3)2 surpasses other representative non-precious metal catalysts recently reported for both OER overpotential and Tafel slope, as presented in Fig. 3g and Table S4. To quantitatively analyze the differences of W18O49/Co3(BO3)2, W18O49, and Co3(BO3)2, we measured the liquid contact angles (LCA) on their surfaces. In electrocatalysis, the wettability of catalysts affects the interaction between the catalysts and electrolytes, which closely relates to their catalytic performance. As seen in Fig. S24, the W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> possesses well water adsorption, which promotes the rapid infiltration of the electrodes and accelerates the migration of the hydroxyl group, thus improving OER activity [16].

Stability is also a crucial parameter for evaluating highly efficient electrocatalysts. The  $W_{18}O_{49}/Co_3(BO_3)_2$  maintains its activity without discernible fluctuations after operating chronopotentiometry (CP) test (over 100 h at 10 mA cm<sup>-2</sup>) and undergoing continuous 5000 cyclic scans (Fig. 3h). The slight attenuation could be caused by the inevitable partial detachment of the catalyst from the conductive substrate, and the gas-evolving process will also exacerbate the partial detachment. In contrast, the Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> catalyst exhibits a rapid performance degradation over time under the same operating conditions, highlighting its poor structural stability in the absence of  $W_{18}O_{49}$ . We detected the dissolved metal content (Co, W, and Ni) in the electrolyte before and after the durability test. The ICP-MS results demonstrate that the  $W_{18}O_{49}$  substrate significantly reduces Co leaching and enhances the structural

stability of  $Co_3(BO_3)_2$  (Fig. S25). Besides, the content of W in  $W_{18}O_{49}/$ Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> undergoes only minor changes, demonstrating the excellent stability of the W<sub>18</sub>O<sub>49</sub> substrate during the reaction process. We further studied the physical and chemical structure of the W18O49/Co3(BO3)2 after a stability test to understand the effect of incorporating W18O49 substrate. After long-term stability, the W18O49/Co3(BO3)2 only retained the diffraction peak of the NF substrate, which may be due to the inevitable partial dissolution and the generation of partial amorphous CoOOH (Fig. S26). Owing to the active CoOOH, the sample still exhibits excellent OER performance. The SEM and TEM images (Fig. S27a-b) reveal that indicate that only slight agglomeration occurred in the catalyst. EDS elemental mappings showed a dispersion of W, Co, B, and O atoms throughout the entire W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> after OER stability (Fig. S27c). For Co 2p XPS spectra of W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, the increase in the Co<sup>3</sup> <sup>+</sup>/Co<sup>2+</sup> ratio indicates the formation of high-valent active species during the reaction process (Fig. S28a). In the O 1 s XPS spectra, the relative content of O<sub>L</sub> and O<sub>V</sub> remains nearly unchanged after the OER stability, which is beneficial for maintaining the structural integrity and catalytic performance of the initial catalyst (Fig. S28b). As a binder-free electrode, the as-synthesized W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> exhibits good activity and durability under alkaline conditions as concluded above.

Such outstanding OER performance motivates us to assemble a water-alkali electrolyzer to evaluate its potential for practical overall water splitting (Fig. S29a). A two-electrode water electrolyzer was constructed by paring the homemade W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> anode with a Pt/C cathode. From the polarization curve in Fig. S29b, W18O49/ Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>||Pt/C delivers cell voltages of 1.51 and 1.67 V to attain the current densities of 10 and 100 mA cm<sup>-2</sup>, respectively. Meanwhile, compared with recently reported noble-metal-free electrocatalysts for overall water splitting, the constructed cell performance stands competitively, as depicted in Table S5. The long-term stability is also a critical checkpoint for its practical utilization, particularly at high current density. W18O49/Co3(BO3)2|Pt/C electrolyzer continuously operated for 140 and 50 h at 100 and 500 mA  $\rm cm^{-2}$  with slight attenuation observed, suggesting its superior electrochemical stability (Fig. S29c-d). These results indicate that the  $W_{18}O_{49}/Co_3(BO_3)_2$  composite is a highly propitious alternative to replace commercial noble metal electrocatalysts for achieving practical overall water splitting.

To understand the dynamic structural evolution and reaction pathway on the heterostructure, a series of in-situ characterizations were used to identify the key intermediates of the reaction active sites during actual OER working conditions. First, in-situ Fourier transform infrared (FTIR) spectra were used to detect the key reaction intermediates during the OER and clarify the mechanism of catalytic reactions. Upon the application of potential, both W18O49/Co3(BO3)2 and  $Co_3(BO_3)_2$  detected a distinct peak around 1108 cm<sup>-1</sup> (Fig. 4a-b), which represents the characteristic vibration of the \*OOH species [49,50]. Noticeably, hump in Fig. 4a arises from the hydrogen bonding interactions of \*OOH with neighbors, leading to modifications in the molecular vibrational behavior [50]. The capture of the \*OOH intermediate specified the four-step absorbate evolution mechanism (AEM) reaction pathway of the catalysts and precluded lattice oxygen mechanisms [51]. In Fig. 4c, as application potential rose, the intensity of \*OOH vibration band recorded on W18O49/Co3(BO3)2 is considerably stronger than that recorded for Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, evidencing a faster oxygen exchange on W18O49/Co3(BO3)2 [52]. Moreover, \*OH at around 3350  $\mathrm{cm}^{-1}$  be detected [53]. To further elucidate the oxygen evolution mechanism that occurs on the W18O49/Co3(BO3)2 and Co3(BO3)2, in-situ differential electrochemical mass spectroscopy (DEMS) measurements were conducted using the isotope <sup>18</sup>O. Fig. 4d-e show the main mass signals of  ${}^{32}O_2$  ( ${}^{16}O^{16}O$ ), followed by  ${}^{34}O_2$  ( ${}^{16}O^{18}O$ ) and  ${}^{36}O_2$  ( ${}^{18}O^{18}O$ ), for the  $W_{18}O_{49}/Co_3(BO_3)_2$  and  $Co_3(BO_3)_2$  with <sup>18</sup>O-labeling during three times of CV in H<sub>2</sub><sup>16</sup>O aqueous alkaline electrolyte, where trace amounts of <sup>34</sup>O<sub>2</sub> product was attributed to the natural isotopic abundance of <sup>18</sup>O in the electrolyte [54,55]. Meanwhile, the intensity of the  ${}^{36}O_2$  signal for both materials was not detected. Conclusively, these results further



**Fig. 4.** Investigating the dynamic structure evolution during OER. In-situ FTIR spectra of (a)  $W_{18}O_{49}/Co_3(BO_3)_2$  and (b)  $Co_3(BO_3)_2$ . (c) Normalized intensity. DEMS signals from the reaction products of <sup>18</sup>O-labeled electrocatalyst in 1.0 M KOH with  $H_2^{16}O$  of (d)  $W_{18}O_{49}/Co_3(BO_3)_2$  and (e)  $Co_3(BO_3)_2$ . (f) Percent contribution of the AEM pathway. (g) In-situ Raman spectrum and (h) the corresponding contour map. (i) Schematic illustration of AEM mechanism.

show that the OER process primarily follows the AEM for both  $W_{18}O_{49}/Co_3(BO_3)_2$  and  $Co_3(BO_3)_2$  electrocatalysts (Fig. 4f-i). In-situ Raman spectra were also recorded at varying potentials. As shown in Fig. 4g-h, with increasing applied positive potentials, the characteristic Raman bands of Co-O gradually disappear, while two  $Co^{3+}$ -O peaks emerge at approximately 463 and 585 cm<sup>-1</sup>, corresponding to the  $E_g$  bending and  $A_{1g}$  stretching vibrations in CoOOH, respectively [32]. It is notable that the emergence of the  $Co^{3+}$ -O Raman peaks of occur at 1.20 V for  $W_{18}O_{49}/Co_3(BO_3)_2$ . On the contrary,  $Co_3(BO_3)_2$  exhibits the remaining general features of Co-O peaks (Fig. S21). Negligible changes could be observed unless at a higher voltage, indicating that there is little formation of CoOOH species at low applied voltages. These results suggest that the formation of heterojunction contributes to the phase evolution during electrochemical activation, thus oxygen evolution activity [56].

To provide a more comprehensive understanding of the dynamic structural changes during operation, a series of XPS test results measured at different potentials were collected to monitor the electronic structure variation of materials (Fig. S30). As observed in Fig. 5c and Fig. S31, detailed quantitative analysis shows the rate of increase in the relative percentage of  $\text{Co}^{3+}/\text{Co}^{2+}$  relative percentage in W<sub>18</sub>O<sub>49</sub>/

 $Co_3(BO_3)_2$  is significantly higher than in  $Co_3(BO_3)_2$  during the reaction process, indicating the rapid formation of a higher-valent active species, in line with in-situ Raman spectra [57]. For the W 4 f spectra, as the voltage increases, the ratio of  $W^{6+}/W^{5+}$  slightly increases and remains stable at 3.57, declaring that the critical role of W<sub>18</sub>O<sub>49</sub> substrate in stabilizing the W18O49/Co3(BO3)2 system (Fig. 5d, Fig. S32, and Table S6). Corresponding to this phenomenon is the O<sub>L</sub>/O<sub>V</sub> ratio obtained from the O 1 s spectra. Fig. 5a,b and e show the variations in the proportion of  $O_{L}/O_{V}.$  The ratio of  $O_{L}/O_{V}$  can be a yardstick to estimate the relative amount of surface oxygen vacancies. A low ratio of  $O_I/O_V$ implies preferential adsorption of water at the intrinsic O<sub>V</sub> sites due to steric hindrance, which is closely connected with optimizing adsorption and desorption of intermediate oxygen species. For  $W_{18}O_{49}/Co_3(BO_3)_2$ , the O<sub>L</sub>/O<sub>V</sub> relative content surges from 0.37 to 0.50 while the potential increases from OCP to 1.5 V. Interestingly, at higher potentials (1.6 V), the O<sub>L</sub>/O<sub>V</sub> ratio almost returns to the initial state (0.38), manifesting that O<sub>V</sub> regeneration, accompanied by oxygen release, stabilizes the active site structure, thereby maintaining activity and stability for subsequent reactions [42]. However, the O 1 s XPS spectra of  $Co_3(BO_3)_2$ evolve in a different trend. Its platforms fail to exhibit satisfactory stability due to rapid surface oxygen exchange kinetics [54], resulting in



Fig. 5. In-situ XPS measurements. In-situ O 1 s XPS spectra for (a)  $W_{18}O_{49}/Co_3(BO_3)_2$  and (b)  $Co_3(BO_3)_2$ . Variations in (c)  $Co^{3+}/Co^{2+}$ , (d)  $W^{6+}/W^{5+}$ , and (e)  $O_L/O_v$  ratios for  $W_{18}O_{49}/Co_3(BO_3)_2$  and  $Co_3(BO_3)_2$  determined from in-situ XPS measurements.

continuous depletion of O<sub>L</sub>. Specifically, the proportion of O<sub>V</sub> gradually increases from OCP to 1.6 V, substantiating that the O<sub>L</sub> in Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> is less reversible. Meanwhile, the EPR results show that the O<sub>V</sub> signal intensity at 1.6 V is nearly identical to that of the initial state in W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, further verifying its reversible nature. As revealed in Fig. S34, compared with W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, there is a noticeable decrease with the applied voltage in the B-O content in single Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, further confirming excessive boron leaching leads to structural instability. This observation aligns with the reversible O<sub>V</sub> in W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, which contribute to its structural stability.

To investigate the coupled relationship between material system,

interfacial reaction, and system performance, the cross-scale analysis and simulation from the microscale to the macroscale through finite element method (FEM) was conducted with this framework (Table S7). FEM was used to establish models at different levels to analyze the electrode surface, half-cell reaction, and the overall water electrolyzer. The  $Co_3(BO_3)_2$  and  $W_{18}O_{49}/Co_3(BO_3)_2$  electrocatalysts were compared to identify their capability of absorption of reactive oxygen species and OER reaction capabilities. Concerning most active  $W_{18}O_{49}/Co_3(BO_3)_2$ catalyst features a significant number of nanosized pores and possesses a smaller d-band center value compared to that of monomer, which largely affects the oxygen adsorption and desorption processes and



**Fig. 6.** FEM analysis on the OER performance of different catalysts. Simulation result of the oxygen production rate for (a)  $Co_3(BO_3)_2$  and (b)  $W_{18}O_{49}/Co_3(BO_3)_2$ . The potentials and current density of electrolytes in the system of (c)  $Co_3(BO_3)_2$  and (d)  $W_{18}O_{49}/Co_3(BO_3)_2$ . The gas pressure distribution diagram of the full cell for (e)  $Co_3(BO_3)_2$  and (f)  $W_{18}O_{49}/Co_3(BO_3)_2$ .

favorably provides higher compatibility with the potential for the OER in alkaline media, a model of the electrode surface as shown in Fig. S35, was established to investigate the difference of oxygen intermediate absorbability based on calculation from Brickman equation [58], after introducing the factors of the specific surface area and the pore size distribution of the electrode materials. It can be found that there are differences in the amount of adsorbed reactive oxygen species on the materials, as indicated by the dotted box in Fig. 6a-b.  $W_{18}O_{49}/Co_3(BO_3)_2$  with relatively more nanosized pores and more oxygen vacancies leading to a high oxygen release rate relative to  $Co_3(BO_3)_2$ , demonstrates the highest concentration of active oxygen at the interface between the electrode material and the electrode surface, reflected from the colorful longitudinal distribution of concentration, indicating its superior adsorption capability of reactive oxygen species.

To further figure the nature of the more efficient electrocatalytic electrochemical catalytic ability of  $W_{18}O_{49}/Co_3(BO_3)_2$ , based on the half-cell reaction model in Fig. S36, the calculation of OER reaction

capabilities of two materials was conducted with incorporation of the current distribution as shown in Fig. 6c,d. It is noted that the  $W_{18}O_{49}/Co_3(BO_3)_2$  has the dense current density distribution with more Faraday processes occurring per unit time as well as fastest gas flow velocity, thus resulting in a more intensive electrolyte current density and a faster rate of oxygen production with an intensification of local vortices on the current surface, which drives the positive OER reaction while carrying away the surface-adhered oxygen, and thus further accelerating the subsequent OER reaction.

Water-splitting devices are very critical for the sustainable production of hydrogen and oxygen through the electrolysis of water [59]. The main challenge for the full electrolysis cell lies in the mismatching of catalytic rates over past years and ideally, the production of 1 molecule of  $O_2$  accompanies the production of 2 molecules of  $H_2$  at the same time frame to achieve a satisfying water electrolysis [60]. However, a slower OER rate would inversely inhibit  $H_2$  production, leading to a huge efficiency degradation of the full cell. Therefore, the above half-cell



**Fig. 7.** DFT calculations. (a) Differential charge density, the yellow and green regions represent electron accumulation and depletion, respectively. (b) The DOS plots, (c) PDOS and band center of Co d-state, (d) the schematic of the optimized bonding behavior, (e) COHP calculations, (f) summary COHP calculations, and (g) calculated energy of Co demetallation for  $W_{18}O_{49}/Co_3(BO_3)_2@CoOOH$  and  $Co_3(BO_3)_2/CoOOH$ . (h) Gibbs free energy profile of OER (The insets are OER mechanism on  $W_{18}O_{49}/Co_3(BO_3)_2@CoOOH$ ).

reaction in combination with the conventional HER system was simulated by the exploration of gas partial pressures to study electrode matching in the case of two various OER samples, which significantly impacted the overall performance of the water electrolyzer (Fig. S37). As exhibited in Fig. 6e,f, it is worth noting that the  $W_{18}O_{49}/Co_3(BO_3)_2$  system with a faster reaction rate exhibits matching partial pressures for HER and OER, indicating a more compatible reaction rate and thus superior device performance. Conversely, the  $Co_3(BO_3)_2$  system with poor performance demonstrates inferior gas transport in the HER, evidenced by the vertical distribution of partial pressure gradient, suggesting the OER reaction rate limits the HER reaction rate, reducing the overall efficiency of the full electrolytic cell.

After thoroughly discussing the structure-activity relationship based on the results of experimental characterizations, the density functional theory (DFT) calculation was conducted to provide theoretical insights into the underlying reaction mechanism in the composite structure to promote the OER activity. The W18O49/Co3(BO3)2@CoOOH and Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>@CoOOH were selected as computational models, supported by the above experimental results (Fig. S38). Fig. 7a provides charge density distribution on the W18O49/Co3(BO3)2@CoOOH heterostructure, where the green region represents the electron depletion, and the yellow region indicates the electron accumulation. It can be clearly seen that the electrons are accumulated in the region of the O atom, while depleted around the Co and W atoms, uncovering that the electron in Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> transfers to the adjacent CoOOH. These results reveal the strong charge interactions between W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> and CoOOH. To further understand the detailed information on the electronic structures, we further demonstrate and calculate the density of states (DOS) and dband center (ed). The total DOS of the W18O49/Co3(BO3)2@CoOOH catalyst shows a higher occupation at the Fermi level (E<sub>F</sub>) compared with Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>@CoOOH (Fig. 7b), suggesting that the electronic coupling reduces the charge transfer resistance to enable swift electron transfer [61–63]. Noticeably, the  $\varepsilon_d$  of W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>@CoOOH (Co) is lower than that of Co3(BO3)2@CoOOH monomer in the projected density of states (PDOS) plot (Fig. 7c). It is shown that the strong electron interaction with the formation of the interface pushes up the downshift of the  $\varepsilon_d$ . Based on the d-band theory, the lower d-band position (keep away from the Ef) results in weaker intermediates adsorption, as the antibonding states are shifted downward (Fig. 7d). The lower antibonding energy states weaken the interaction between the intermediates and the catalytic active sites, thus optimizing the adsorption-free energy and facilitating the subsequent reaction steps [64]. Additionally, the bond strength between the Co sites and \*OOH, was assessed via crystal orbital Hamiltonian population (COHP). The positive and negative COHP imply the anti-bonding states and the bonding states, respectively. The bonding states of Co-OOH bond in W<sub>18</sub>O<sub>49</sub>/Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>@CoOOH are much larger under the Fermi level than Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>@CoOOH, suggesting the adsorption ability of \*OOH in  $W_{18}O_{49}/Co_3(BO_3)_2$ @CoOOH is optimal, thereby enhancing the intrinsic activity (Fig. 7e-f and Table S8) [46]. The energy changes associated with the dissolution process of surface Co atoms from both W18O49/Co3(BO3)2@CoOOH and Co3(BO3)2@CoOOH were evaluated, given that the demetalization of surface Co species could be a contributing factor to the diminished activity and stability of catalysts. As illustrated in Fig. 7g, the energy barrier for Co demetalization increased from 2.49 to 3.22 eV with the incorporation of the W<sub>18</sub>O<sub>49</sub> component, suggesting a more stable surface Co in W18O49/CO3(BO3)2@CoOOH than Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>@CoOOH, in accordance with the in-situ O 1 s results. The formation of the interface can induce strong electron interactions, thereby highly activating the active sites and the interface. Four-electron OER pathways based on the AEM were further studied by calculating and comparing the Gibbs free energy diagram of the corresponding adsorption intermediates (\*OH, \*O, and \*OOH) on the active sites (Fig. 7h). The high formation barrier of \*OOH, with calculated Gibbs free energies ( $\Delta G_{*OOH}$ ) of 2.66 eV for Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>/CoOOH, as a rate-determining step (RDS) restricts the OER activity of catalysts.

Notably, the RDS of  $W_{18}O_{49}/Co_3(BO_3)_2@CoOOH$  shifts to the former step of \*OOH formation–specifically, \*O formation, suggesting energy injection is significantly reduced to 1.54 eV (Table S9). It's concluded that the  $W_{18}O_{49}/Co_3(BO_3)_2@CoOOH$  breaks the typical barrier limitation (\*OOH formation), which is greatly facilitated by the strong interfacial electronic interaction. From a theoretical perspective, we demonstrate that strong electron interactions at the interface modulate the dynamic adsorption and dissociation of intermediates during the process, which is crucial for accelerating the oxygen evolution kinetics.

## 3. Conclusion

We demonstrate the interfacial modulation as well as its triggered reversible oxygen vacancies together enhance the intrinsic activity and stability of  $W_{18}O_{49}/Co_3(BO_3)_2$ . The optimized  $W_{18}O_{49}/Co_3(BO_3)_2$  displays a low overpotential of 251 mV at 10 mA cm<sup>-2</sup> and retains long-term durability exceeding 100 h. The incorporation of  $W_{18}O_{49}$  facilitates the formation of active centers and charge transfer to improve oxygen evolution activity. It is validated that the presence of reversible oxygen vacancies maintains Co active sites, enabling crystal structure stability under working potentials verified by in-situ characterization techniques. Theoretical studies show that a highly active interface optimizes the adsorption of oxygenated intermediates, shifting the RDS from \*OOH formation to \*O formation. The concepts of interface engineering and fabrication of reversible oxygen species not only offer paths to the next-generation OER catalysts but also illustrate a promising way to design stable active sites for nanocatalysts.

#### **CRediT** authorship contribution statement

Sun Tianxiao: Writing – original draft, Investigation. Zhu Jianqiu: Visualization, Data curation. Wei Fengli: Writing – original draft, Methodology, Investigation. Peng Qimin: Writing – original draft, Methodology. Sun Shuhui: Writing – review & editing, Visualization, Supervision. Yang Xiulin: Writing – review & editing, Visualization, Supervision, Conceptualization. Wu Bin: Writing – review & editing, Supervision. Luo Zuyang: Investigation, Data curation. Wang Dingsheng: Validation, Data curation.

## **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. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2025.110961.

#### Nano Energy 139 (2025) 110961

## Data availability

The data that has been used is confidential.

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