

Interfacial electric field regulates surface water environment in RuO₂ coated Co₃O₄ for proton exchange membrane water electrolysis

Yuelong Mao, Yang Xu, Ruirui Yu, Suqian Liu, Haijun Li, Shaomin Wang(✉), Hongnan Jia(✉), Jingzhen Du(✉)
College of Chemistry, Zhengzhou University, Zhengzhou 450001, China

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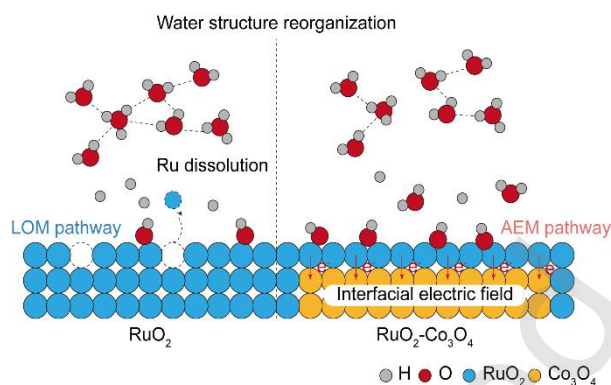
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This work demonstrates that RuO_2 -coated Co_3O_4 achieves high atom utilization in PEMWE device operation. The engineered interfacial electric field not only activates and stabilizes Ru active sites but also optimizes the $^*\text{OH}$ coverage and interfacial water structure.

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College of Chemistry, Zhengzhou University, Zhengzhou 450001, China

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✉ Address correspondence to Shaomin Wang, wshaomin@zzu.edu.cn; Hongnan Jia, hongnanjia@zzu.edu.cn; Jingzhen Du, jingzhendu@zzu.edu.cn

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ABSTRACT: Designing Ru-based anodic catalysts to substitute Ir in proton exchange membrane water electrolysis (PEMWE) is pivotal to slashing hydrogen generation expenses. Herein, a conformal coating of RuO₂ has been uniformly deposited over Co₃O₄ nanocrystals (RuO₂-Co₃O₄) to enhance the utilization efficiency and durability of ruthenium for acidic oxygen evolution reaction (OER). Structural characterizations and density functional theory (DFT) calculations reveal that Co₃O₄ regulates the electronic structure of the surface RuO₂ through Ru-O-Co motifs, activating the Ru sites while inhibiting the participation of lattice oxygen by lowering the energy level of O 2p band. As expected, unlike commercial RuO₂, the RuO₂-Co₃O₄ catalyst switches to a robust adsorbate evolution mechanism pathway, as evidenced by electrochemical and *in situ* differential electrochemical mass spectrometry (DEMS) results. Remarkably, benefiting from the interfacial electric field between RuO₂ and Co₃O₄, the RuO₂-Co₃O₄ displays an enhanced *OH coverage and improved proportion of free-H₂O in the electric-double-layer region, which are responsible for the improved acidic OER kinetics. Consequently, the obtained RuO₂-Co₃O₄ displays a high mass activity of 376.6 A g⁻¹, which is 27-fold higher than that of the commercial RuO₂. When implemented in PEMWE devices, a current density of 500 mA cm⁻² is achieved with only 1.75 V under an extremely low catalyst loading of 0.15 mgRu cm⁻².

KEYWORDS: acidic oxygen evolution reaction; core-shell heterostructure; interfacial electric field; electric-double-layer region; proton exchange membrane water electrolysis

1 INTRODUCTION

Proton exchange membrane water electrolysis (PEMWE) represents a promising technology for renewable energy conversion and storage in the form of hydrogen, offering significant potential in sustainable systems [1-3]. Compared to the hydrogen evolution reaction (HER), oxygen evolution reaction (OER) at the anode is a critical four-proton-coupled electron transfer process, governing the overall water-splitting reaction [4, 5]. Breakthroughs in material development and advanced insights into reaction kinetics will be pivotal for overcoming the obstacles of high overpotentials and sluggish kinetics in electrocatalytic OER. Until now, scarce iridium oxides (IrO_x) have been regarded as the commercial anode catalyst operating in harsh acidic environments due to the optimal balance between activity and stability [6-8]. Recently, ruthenium oxide (RuO₂) has emerged as a viable alternative, attracting attention for its satisfactory intrinsic activity [9, 10]. Nevertheless, the generation of lattice oxygen vacancies and dissolution of Ru species usually result in the collapse of the crystal structure of RuO₂ and degraded stability, thereby inhibiting the large-scale application [11, 12]. Consequently, developing Ru-based catalysts with high stability and high

atomic utilization to reduce the reliance on precious metals is the key to the large-scale deployment of PEMWE.

Various strategies, such as heteroatom doping [13-16], defect engineering [17-19], heterojunction construction [20-24], have been reported to enhance the efficiency and durability of Ru-based catalysts by i) modulating the electronic structure, charge distribution and coordination environment of Ru active sites [25, 26], ii) manipulating the adsorption and desorption kinetics of key intermediates (such as *O, *OOH) [27, 28], and regulating reaction pathway from the lattice oxygen oxidation mechanism (LOM) to the adsorbate evolution mechanism (AEM) [29]. Despite these advances, simultaneously promoting the catalytic activity and stability of Ru-based catalysts by conventional methods still remains challenging. Recently, Chen et al. reported an epitaxial growth of IrO_x on Co₃O₄, which enables efficient Ir utilization in acidic OER *via* Ir-O-Co interfacial bonding, which modulates intermediate adsorption energies for enhanced performance and structural stability [30], implying the application potential of the coating strategy [31]. Inspired by this, coating RuO₂ onto Co₃O₄ holds promise to stabilize Ru sites *via* built-in electric fields while maximizing active site utilization. However, the feasibility of this specific configuration for acidic OER has rarely been explored,

necessitating further in-depth investigation.

In addition, the dynamic structure and reaction behavior at the interfacial electric double layer (EDL) region further contribute to the complexity of OER [32-35]. For instance, Zhai and co-workers enhanced the hydrogen-bonding interactions by introducing hydrophilic nitrogen-doped carbon layers, thereby improving the adsorption and deprotonation of water molecules [36]. García de Arquer et al. incorporated high-valence sacrificial elements into the Co_3O_4 lattice to capture and stabilize water molecules and hydroxide ions, making the dissolution of cobalt ions thermodynamically unfavorable [37]. Additionally, Peng's group discovered that the incorporation of La reduces the strength of local hydrogen-bonding networks, alleviating excessive polarization of Co-O bonds by water molecules, thereby increasing the energy barriers for bond cleavage and cobalt dissolution [38]. However, research on the EDL environment in interfacial systems remains limited, and further investigation is needed to understand how the interfacial electric field influences the water-catalyst interface.

In this work, we have uniformly deposited an ultrathin coating of RuO_2 over Co_3O_4 nanocubes (denoted as $\text{RuO}_2\text{-Co}_3\text{O}_4$) to significantly enhance the utilization efficiency and durability of ruthenium for the acidic OER. Combined with *in situ* spectroscopic investigations and theoretical studies, we discovered that Co_3O_4 not only dynamically regulates the adsorption capacity of RuO_2 active sites toward oxygen-containing species but also effectively drives the Ru sites to follow the AEM pathway, thereby suppressing the undesirable participation of lattice oxygen. Notably, *in situ* attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) revealed that the interfacial electric field generated between RuO_2 and Co_3O_4 plays a crucial role in disrupting the continuity of the interfacial hydrogen-bonding network, which promotes the transfer and dissociation of free water molecules and facilitates the activation of oxygen-containing intermediates. Consistent with these mechanistic insights, the $\text{RuO}_2\text{-Co}_3\text{O}_4$ catalyst demonstrates exceptional electrocatalytic performance, achieving a current density of 10 mA cm^{-2} at an overpotential of only 222 mV, while exhibiting a remarkably high mass activity of 376.6 A g^{-1} at 1.54 V vs. RHE (approximately 27-fold higher than commercial RuO_2 (Com- RuO_2)). Furthermore, when integrated into PEMWE devices, the catalyst delivers a current density of 500 mA cm^{-2} at a cell voltage of 1.75 V with an extremely low ruthenium loading of $0.15 \text{ mg}_{\text{Ru}} \text{ cm}^{-2}$. This work provides fundamental insights into core-shell electrocatalyst design, elucidating the role of interfacial engineering in optimizing reaction pathways and water structure to achieve high ruthenium efficiency, superior activity, and durability for PEMWE anodes.

2. EXPERIMENTAL SECTION

2.1 Chemicals.

Cobalt nitrate hexahydrate (99.99 %) was purchased from

Beijing Innochem Technology Co., Ltd. XC-72R was purchased from Suzhou Sinero Technology Co., Ltd. Sodium hydroxide was purchased from Tianjin Yongda Chemical Reagent Co., Ltd. Ruthenium(III) chloride was purchased from Shanghai Haohong Bio-pharmaceutical Technology Co., Ltd. Nafion® 117 solution (~5 wt%) in a mixture of Beijing innochem Technology Co., Ltd. Sulfuric acid (H_2SO_4) and Anhydrous ethanol were purchased from Luoyang Chemical Reagent Factory. The ultrapure water ($18.25 \text{ M}\Omega \text{ cm}$) prepared from an ultrapure-water purification system (Ulupure) was used throughout the whole experiment.

2.2 Synthesis of Co_3O_4 .

The precursor $\text{Co}(\text{OH})_2$ for Co_3O_4 was synthesized *via* a hydrothermal method. Briefly, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.04 mol) and NaOH (0.01 mol) were ultrasonically dissolved into ultrapure water (10 mL) to prepare solutions **A** and **B**, respectively. Then, solution **B** was added dropwise to solution **A** with stirring, and then stirred for 5 minutes. The mixture was sealed into a 50 mL polytetrafluoroethylene (Teflon)-lined stainless steel autoclave and heated at 180°C for 5 hours. After the reaction, the product was collected, washed sequentially with deionized water and ethanol (3 cycles), and dried at 60°C for 12 h. Subsequently, 300 mg of the obtained $\text{Co}(\text{OH})_2$ was evenly placed in a porcelain boat, followed by calcination at 500°C for 3 h in air with a heating rate of 5°C min^{-1} .

2.3 Synthesis of $\text{RuO}_2\text{-Co}_3\text{O}_4$.

To synthesize the $\text{RuO}_2\text{-Co}_3\text{O}_4$ catalyst, 10 mg of RuCl_3 was dissolved in 0.4 mL of ultrapure water and dropwise added to 100 mg of Co_3O_4 support. The obtained mixture was uniformly ultrasonicated for 30 min and dried at 60°C for 12 h, followed by calcination at 350°C for 5 h in air atmosphere with a heating rate of 5°C min^{-1} .

3. RESULTS AND DISCUSSION

3.1 Synthesis and Structural Characterization.

The synthetic process of the $\text{RuO}_2\text{-Co}_3\text{O}_4$ catalyst is schematically shown in Figure 1a. Briefly, the $\text{RuO}_2\text{-Co}_3\text{O}_4$ electrocatalyst was prepared through a facile incipient wetness impregnation method using Co_3O_4 as support, with specific steps detailed in the experimental section. We first surveyed the phase structure and morphology of Co_3O_4 precursor by powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM). As shown in Figure S1, the diffraction pattern of as-prepared Co_3O_4 is well-indexed to the standard face-centered cubic Co_3O_4 (PDF#42-1467). Besides, the obtained Co_3O_4 exhibits a nanocube morphology, with the uniformly distributed Co and O elements (Figure S2), indicating the successful synthesis of Co_3O_4 support. By controlling the concentration of RuCl_3 in the impregnation solution, the ultrathin RuO_2 coated Co_3O_4 was prepared, and the Ru/ (Ru + Co) atomic fraction was only 2.1 %, as evidenced by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (Table S1). The

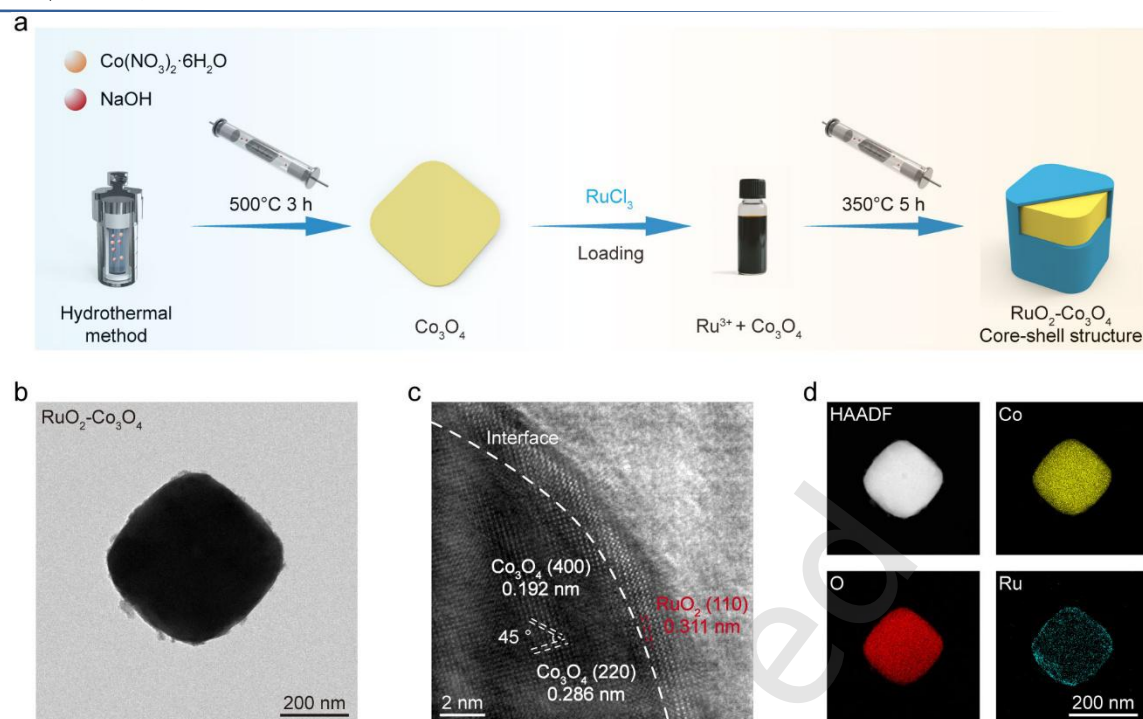


Figure 1 Structural characterization of $\text{RuO}_2\text{-Co}_3\text{O}_4$ electrocatalyst. (a) Schematic illustration of the synthesis of $\text{RuO}_2\text{-Co}_3\text{O}_4$ catalyst. (b) TEM image of $\text{RuO}_2\text{-Co}_3\text{O}_4$. (c) HAADF-STEM image of $\text{RuO}_2\text{-Co}_3\text{O}_4$. (d) Element mapping images corresponding to $\text{RuO}_2\text{-Co}_3\text{O}_4$ catalyst.

morphology and PXRD pattern of $\text{RuO}_2\text{-Co}_3\text{O}_4$ are similar to those of pure Co_3O_4 , which may be attributed to the ultrathin nature of the RuO_2 coating (Figures 1b and S1). To further investigate the morphology of RuO_2 -coated Co_3O_4 , high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was employed. As shown in Figure 1c, lattice fringes corresponding to the (400) and (220) crystal planes of Co_3O_4 were observed in the inner layer of the $\text{RuO}_2\text{-Co}_3\text{O}_4$ surface, with spacings of 0.192 nm and 0.286 nm, respectively [39]. In the outer surface layer, the (110) crystal plane of RuO_2 was measured, with an interplanar spacing of 0.311 nm [9]. The core-shell heterostructure was also affirmed through energy-dispersive X-ray spectroscopic (EDS) elemental mapping of $\text{RuO}_2\text{-Co}_3\text{O}_4$ (Figure 1d), revealing a uniform distribution of Ru and O elements in the ultrathin RuO_2 shell.

To gain deeper insights into the valence state and distinctive electronic structure of the $\text{RuO}_2\text{-Co}_3\text{O}_4$ electrocatalysts, X-ray absorption spectroscopy (XAS) was performed (Figure 2a). As shown in Figure 2a, the absorption edge of the Co K-edge X-ray absorption near-edge structure (XANES) spectra for $\text{RuO}_2\text{-Co}_3\text{O}_4$ shifts to a lower energy compared to the pristine Co_3O_4 . This suggests that the average oxidation state of the Co species in $\text{RuO}_2\text{-Co}_3\text{O}_4$ is lower than uncoated Co_3O_4 , indicating the electron transfer from RuO_2 phase to Co_3O_4 phase. The Co K-edge extended X-ray absorption fine structure (EXAFS) spectrum of Co_3O_4 shows distinct peaks at 1.3, 2.5, and 3.3 Å, corresponding to Co-O, Co- Co_{oct} , and Co- Co_{tet} bonds, respectively (Figure 2b) [40]. For $\text{RuO}_2\text{-Co}_3\text{O}_4$, the Co-O bond length slightly increases compared to Co_3O_4 , indicating that the lattice distortion of Co_3O_4 induced by the RuO_2 coating leads to elongation of the Co-O bond. Furthermore, wavelet transform analysis at the Co K-edge (Figure S3) shows that, compared to Co_3O_4 , the maximum intensity of Co-O coordination in $\text{RuO}_2\text{-Co}_3\text{O}_4$ shifts positively, indicating an increased Co-O bond distance, which confirms the

formation of Ru-O-Co bonds between Ru and the Co-O bonds on the Co_3O_4 surface in $\text{RuO}_2\text{-Co}_3\text{O}_4$. The fitted k^2 -weighted Co K-edge EXAFS spectrum of $\text{RuO}_2\text{-Co}_3\text{O}_4$ (Figure S4) gives a Co-O bond length of 1.92 Å (Table S2), which is longer than that in Co_3O_4 (1.90 Å), suggesting that the covalency of the Co-O bond is weakened due to bond elongation. Evidently, the RuO_2 coating modulates the local electronic and atomic structure of the Co-O bond; specifically, the elongation of Co-O in the Ru-O-Co moiety weakens the Co-O bond covalency and introduces Ru atoms to synergistically interact with Co-O, thereby directly affecting OER performance. X-ray photoelectron spectroscopy (XPS) results are shown in Figures 2c and 2d. The Co 2p XPS of $\text{RuO}_2\text{-Co}_3\text{O}_4$

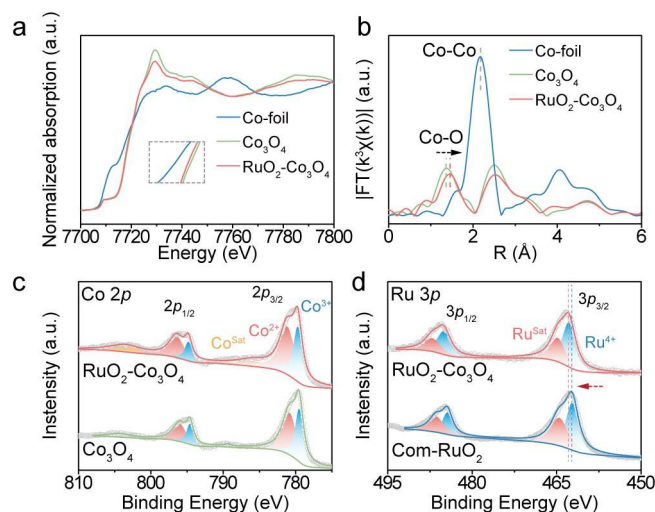


Figure 2 Electronic structure characterization. (a) Normalized Co K-edge XANES spectra. (b) Fourier transforms of Co K-edge EXAFS oscillations for Co-foil, Co_3O_4 and $\text{RuO}_2\text{-Co}_3\text{O}_4$ (c) Co 2p XPS spectra of Co_3O_4 and $\text{RuO}_2\text{-Co}_3\text{O}_4$. (d) Ru 3p XPS spectra of $\text{RuO}_2\text{-Co}_3\text{O}_4$ and Com-RuO_2 .

exhibits a higher $\text{Co}^{2+}/\text{Co}^{3+}$ ratio (Figure 2c) compared to Co_3O_4 , which suggests a lower oxidation state of Co in the $\text{RuO}_2\text{-Co}_3\text{O}_4$ catalyst, consistent with the XAS results, whereas the Ru 3p XPS spectrum of $\text{RuO}_2\text{-Co}_3\text{O}_4$ shifts to a higher binding energy than Com- RuO_2 , along with the increased valence state due to the adjusted electronic structure by Ru-O-Co motifs (Figure 2d).

3.2 OER performance and PEMWE evaluation.

The electrocatalytic OER performance of the $\text{RuO}_2\text{-Co}_3\text{O}_4$ was evaluated in 0.5 M H_2SO_4 using a standard three-electrode configuration. As shown in Figure 3a, the $\text{RuO}_2\text{-Co}_3\text{O}_4$ displays a superior catalytic activity compared to Co_3O_4 and Com- RuO_2 . Specifically, $\text{RuO}_2\text{-Co}_3\text{O}_4$ exhibits the lowest overpotential of 222 mV at a current density of 10 mA cm^{-2} , significantly outperforming Com- RuO_2 (275 mV) (Figure 3b). The Tafel slopes were calculated to assess the reaction kinetics of electrochemical OER on the catalysts (Figure 3c). $\text{RuO}_2\text{-Co}_3\text{O}_4$

shows a lower Tafel slope of 87.4 mV dec^{-1} than Com- RuO_2 ($112.7 \text{ mV dec}^{-1}$), indicating its superior OER kinetics [41]. Encouraged by the extremely low Ru content enabled by the unique core-shell structure, we summarized the mass activity curves of Com- RuO_2 and $\text{RuO}_2\text{-Co}_3\text{O}_4$ electrocatalysts during OER catalysis (Figure 3d). It is worth noting that $\text{RuO}_2\text{-Co}_3\text{O}_4$ exhibits a high mass activity of 376.6 A g^{-1} at $1.54 \text{ V}_{\text{RHE}}$, which is 27-fold higher than commercial RuO_2 (13.9 A g^{-1}). Furthermore, the electrochemically active surface area (ECSA) was estimated by measuring the double-layer capacitance (C_{dl}), as shown in Figures S5 and 3e [42]. Compared to Com- RuO_2 , the $\text{RuO}_2\text{-Co}_3\text{O}_4$ electrocatalyst exhibits a higher C_{dl} value of 10.8 mF cm^{-2} (vs. 4.0 mF cm^{-2} for Com- RuO_2), confirming its larger ECSA and more abundant exposed active sites, which are directly attributed to the high surface area enabled by the core-shell structure. Figure S6 presents the Nyquist plots derived from electrochemical impedance spectroscopy (EIS) tests. The diameters of the semicircles decrease from RuO_2 to $\text{RuO}_2\text{-Co}_3\text{O}_4$.

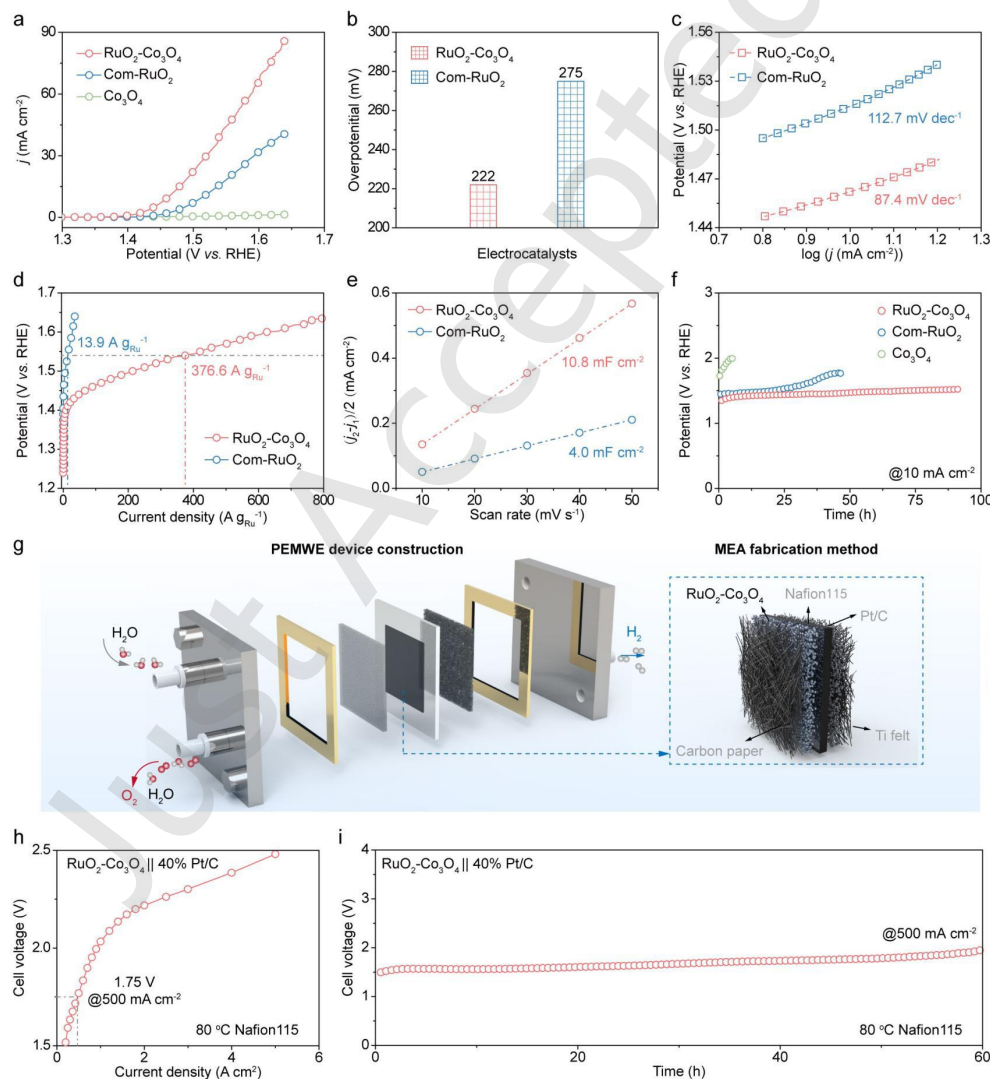


Figure 3 OER evaluation and PEMWE performance of $\text{RuO}_2\text{-Co}_3\text{O}_4$. (a) Polarization curves of the as-prepared Co_3O_4 , Com- RuO_2 and $\text{RuO}_2\text{-Co}_3\text{O}_4$. (b) Corresponding overpotentials at 10 mA cm^{-2} . (c) Corresponding Tafel plots. (d) Mass activity of $\text{RuO}_2\text{-Co}_3\text{O}_4$ and Com- RuO_2 . (e) C_{dl} values of $\text{RuO}_2\text{-Co}_3\text{O}_4$ and Com- RuO_2 . (f) Chronopotentiometry measurements of $\text{RuO}_2\text{-Co}_3\text{O}_4$ at current density of 10 mA cm^{-2} , with Co_3O_4 and Com- RuO_2 as comparison. (g) Schematic diagram of PEMWE along with catalyst-coated membrane. (h) The PEMWE-based polarization curves of $\text{RuO}_2\text{-Co}_3\text{O}_4$. (i) The chronopotentiometry stability test of $\text{RuO}_2\text{-Co}_3\text{O}_4$ at 500 mA cm^{-2} of current density in PEMWE at 80°C temperature.

Co_3O_4 , indicating an improvement in electron transfer capability for the $\text{RuO}_2\text{-Co}_3\text{O}_4$. In detail, the impedance value of $\text{RuO}_2\text{-Co}_3\text{O}_4$ was calculated to be $15.12\ \Omega$, much lower than that of Com-RuO_2 ($64.25\ \Omega$), Table S3, confirming that the interfacial electric field effectively reduces the interfacial charge-transfer barrier. In addition, the *in situ* EIS measurement at different applied voltages was employed to investigate the electrocatalytic kinetics during the OER process (Figure S6) [43, 44]. When the operating voltage is increased from 1.29 V to 1.53 V, $\text{RuO}_2\text{-Co}_3\text{O}_4$ exhibits a significant phase-angle decay in the low-frequency region compared to Com-RuO_2 , demonstrating the presence of an interfacial electric field between RuO_2 and Co_3O_4 , mediated by Ru-O-Co motifs, therefore significantly reducing the interfacial charge-transfer resistance. Considering the poor stability of commercial RuO_2 during acidic water oxidation, the durability of the as-prepared $\text{RuO}_2\text{-Co}_3\text{O}_4$ was evaluated in 0.5 M H_2SO_4 . As shown in Figure 3f, $\text{RuO}_2\text{-Co}_3\text{O}_4$ exhibits nearly unaltered OER performance during the chronopotentiometric test over a period of 90 h at $10\ \text{mA cm}^{-2}$, which is better than Com-RuO_2 (25 h) and Co_3O_4 (5 h). Moreover, $\text{RuO}_2\text{-Co}_3\text{O}_4$ maintains stability in crystallinity, morphology and electronic state after OER cycling test, as evidenced by the unaltered PXRD pattern, HRTEM image and

XPS spectrum (Figures S7-S9). Electrolyte samples taken at 1, 4, and 10 h during chronopotentiometry ($10\ \text{mA cm}^{-2}$) were analyzed to quantify metal dissolution. For $\text{RuO}_2\text{-Co}_3\text{O}_4$, the Ru component demonstrated exceptional stability with a dissolved mass fraction of only 2.6 % relative to its initial loading after 10 hours. In contrast, the Co component showed a higher dissolution of approximately 10%, which may be attributed to minor electrolyte penetration through surface defects or grain boundaries of the RuO_2 shell. Nevertheless, compared to the severe Ru leaching (22.8%) observed in Com-RuO_2 under identical conditions, the significantly suppressed Ru dissolution in our core-shell structure confirms that the RuO_2 coating effectively protects the active sites and maintains structural integrity. To evaluate the application potential of the $\text{RuO}_2\text{-Co}_3\text{O}_4$ catalyst, a membrane electrode assembly (MEA) was fabricated, and the performance of a PEMWE was tested. $\text{RuO}_2\text{-Co}_3\text{O}_4$ and commercial Pt/C catalysts were sprayed onto both sides of a PEM (Nafion 115) with an area of $1\ \text{cm}^2$. Pt-plated titanium felt and carbon paper were used as the gas diffusion layers for the anode and cathode, respectively. The Pt-plated titanium felt was pressed against the membrane side coated with $\text{RuO}_2\text{-Co}_3\text{O}_4$ catalyst, and the carbon paper was pressed against the side coated with Pt/C cathode catalyst to complete

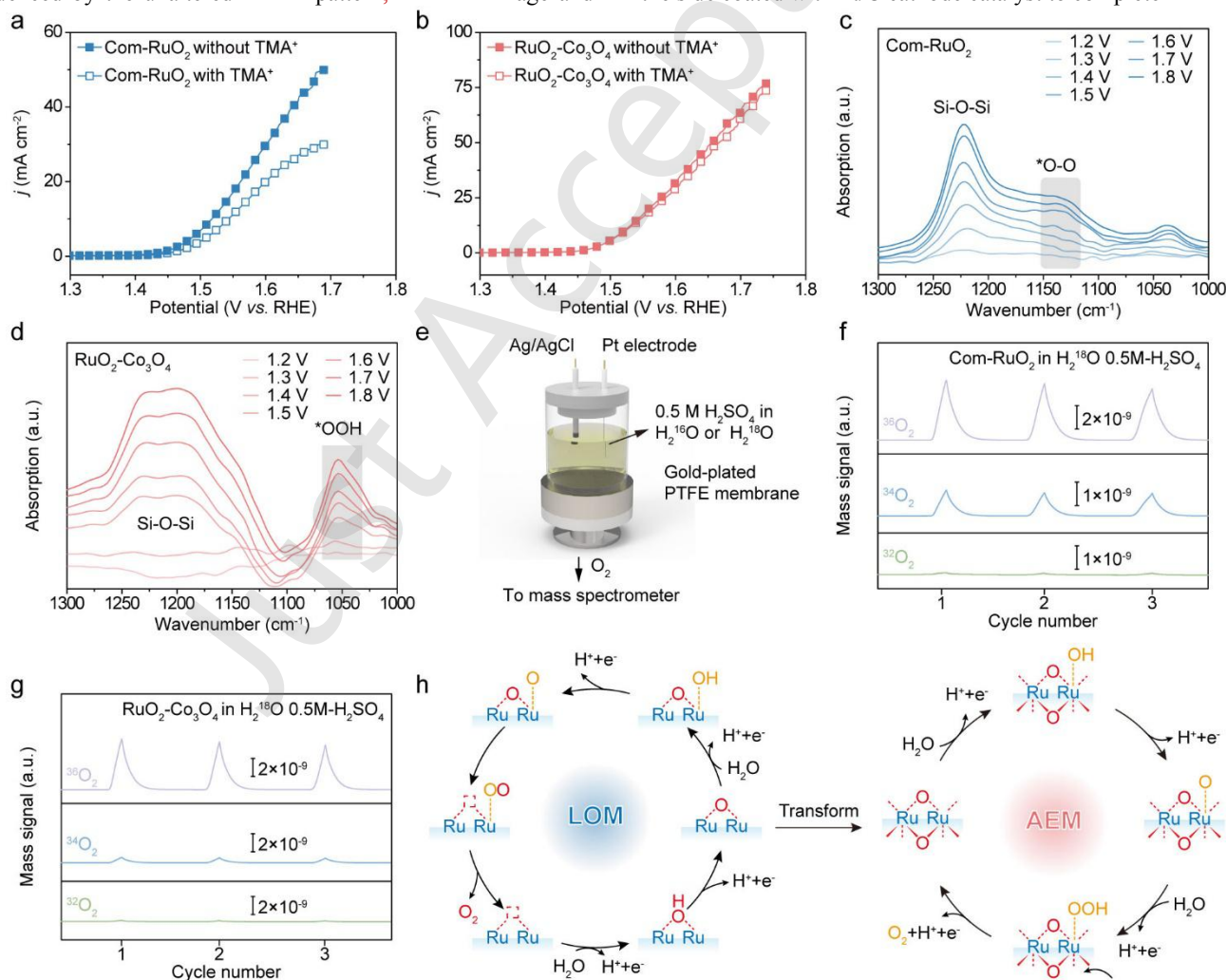


Figure 4 Investigation of OER mechanism. (a, b) Polarization curves of Com-RuO_2 and $\text{RuO}_2\text{-Co}_3\text{O}_4$ under 0.5 M H_2SO_4 electrolyte with or without adding TMA^+ . (c, d) *in situ* ATR-SEIRAS spectra of Com-RuO_2 and $\text{RuO}_2\text{-Co}_3\text{O}_4$. (e) Schematic illustration of DEMS measurement. (f, g) DEMS signals of O_2 products for Com-RuO_2 and $\text{RuO}_2\text{-Co}_3\text{O}_4$. (h) Schematic illustration of LOM and AEM for $\text{RuO}_2\text{-Co}_3\text{O}_4$ the MEA fabrication (Figure 3g). Figure 3h shows the polarization curve of the PEMWE at $80\ ^\circ\text{C}$, achieving a current

density of 500 mA cm^{-2} at 1.75 V (Figure 3h), and stable operation for over 400 h at 100 mA cm^{-2} (Figure S11). Even at 500 mA cm^{-2} , the PEMWE device could work stably for more than 60 h (Figure 3i), demonstrating excellent stability and promising industrial application potential. In summary, the $\text{RuO}_2\text{-Co}_3\text{O}_4$ catalyst exhibits remarkable OER activity, mass activity, and stability, which are comparable to those of the most advanced OER catalysts reported to date (Table S4).

3.3 Mechanistic Insights.

We further investigated the reaction kinetics by electrochemical and spectroscopic techniques to verify the pathway. The LSV curves of Com-RuO₂ and $\text{RuO}_2\text{-Co}_3\text{O}_4$ in 1.0 M tetramethylammonium chloride (TMACl) are compared in Figure 4a and 4b. Typically, TMA^+ ions strongly bind to negatively charged oxygen-containing species generated during the OER, thereby suppressing OER activity in the LOM-based catalysts [45, 46]. Compared to $\text{RuO}_2\text{-Co}_3\text{O}_4$, the sharp current decay of Com-RuO₂ indicates that TMA^+ blocks more reactive oxygen species during the LOM process, implying the altered proton diffusion characteristics and the OER mechanism for $\text{RuO}_2\text{-Co}_3\text{O}_4$. *In situ* ATR-SEIRAS was further employed to identify reaction intermediates during the OER. For Com-RuO₂ at high overpotentials, a distinct absorption band appears at

$\sim 1200 \text{ cm}^{-1}$ (Figure 4c), attributed to the stretching vibration of the $\ast\text{OO}$ intermediate [25, 47]. This suggests that the OER process on Com-RuO₂ at high overpotentials is predominantly governed by a sequential LOM mechanism, leading to faster dissolution and poorer stability. In contrast, the spectra of $\text{RuO}_2\text{-Co}_3\text{O}_4$ show that the vibrational band of the key $\ast\text{OOH}$ intermediate ($\sim 1050 \text{ cm}^{-1}$) appears at $\sim 1.2 \text{ V}$ (Figure 4d) and significantly intensifies with increasing potential, indicating that $\text{RuO}_2\text{-Co}_3\text{O}_4$ most likely follows the AEM pathway [48, 49].

To further confirm the catalytic mechanisms of Com-RuO₂ and $\text{RuO}_2\text{-Co}_3\text{O}_4$, *in situ* DEMS and isotope labeling measurements were performed (Figure 4e). Com-RuO₂ and $\text{RuO}_2\text{-Co}_3\text{O}_4$ were loaded onto a gold-plated hydrophobic gas-permeable membrane and subjected to three linear sweep voltammetry cycles in 0.5 M H_2SO_4 electrolyte prepared with H_2^{18}O . As shown in Figure 4f, Com-RuO₂ produces only $^{36}\text{O}_2$ and $^{34}\text{O}_2$ in each cycle, with a relatively high ratio of $^{34}\text{O}_2$ to $^{36}\text{O}_2$, providing direct evidence for the LOM mechanism [50]. In contrast, $\text{RuO}_2\text{-Co}_3\text{O}_4$ also produces only $^{36}\text{O}_2$ and $^{34}\text{O}_2$, but with a lower ratio of $^{34}\text{O}_2$ to $^{36}\text{O}_2$, indicating that the AEM mechanism dominates on $\text{RuO}_2\text{-Co}_3\text{O}_4$ (Figure 4g) [51]. Subsequently, the ^{18}O -labeled samples were subjected to three additional linear sweep voltammetry cycles in 0.5 M

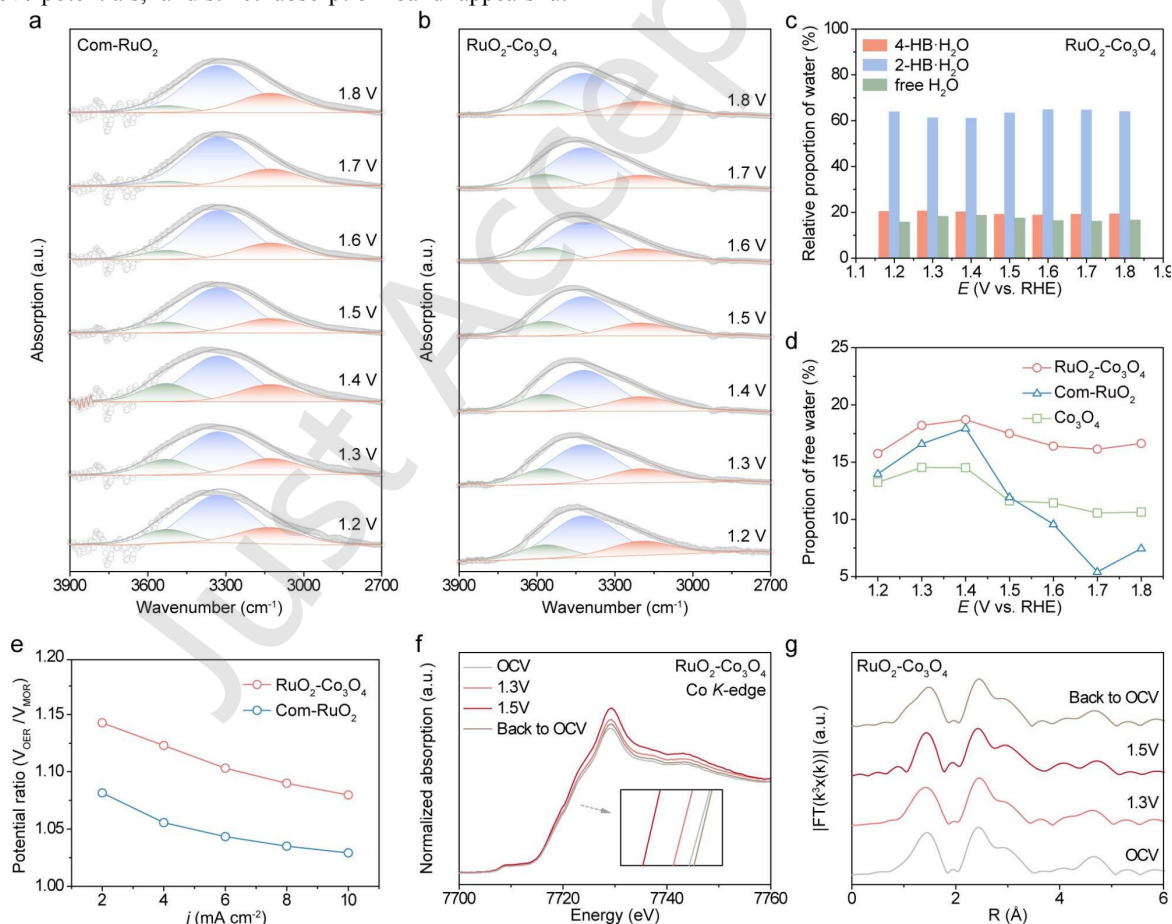


Figure 5 Interfacial electric field mediated EDL optimization. (a,b) Potential-dependent absorption strength of interfacial water through *in situ* ATR-SEIRAS in 0.5 M H_2SO_4 electrolyte for Com-RuO₂ (a) and $\text{RuO}_2\text{-Co}_3\text{O}_4$ (b) catalysts on the Au electrode. 4-HB-H₂O, 2-HB-H₂O, and free-H₂O are shown in red, blue and green, respectively. (c) The proportions of different types of water for $\text{RuO}_2\text{-Co}_3\text{O}_4$ catalysts, derived from (b). (d) The proportions of free-H₂O at varied potentials of Com-RuO₂, Co_3O_4 and $\text{RuO}_2\text{-Co}_3\text{O}_4$ respectively. (e) Potential ratio ($V_{\text{OER}}/V_{\text{MOR}}$) for Com-RuO₂ and $\text{RuO}_2\text{-Co}_3\text{O}_4$ at different current densities. (f,g) *In situ* Co K-edge XANES (f) and corresponding EXAFS data (g) of $\text{RuO}_2\text{-Co}_3\text{O}_4$, at OCV, $1.3 \text{ V}_{\text{RHE}}$, $1.5 \text{ V}_{\text{RHE}}$ and Back to OCV, respectively.

H₂SO₄ prepared with H₂¹⁶O (Figure S12). The results show that neither Com-RuO₂ nor RuO₂-Co₃O₄ produces a ³⁶O₂ signal, demonstrating that neither catalyst follows the oxide path mechanism. Benefiting from the construction of interfacial electric field between inner Co₃O₄ and coated RuO₂ layer, the Ru active sites are effectively activated and tuned to AEM pathway during OER process (Figure 4h), explaining the catalyst's high activity and stability.

3.4 Interfacial electric field mediated EDL optimization.

To elucidate the involvement of proton transfer in the rate-determining step (RDS), kinetic isotope effects (KIEs) were investigated using H/D isotope labeling. Both Com-RuO₂ and RuO₂-Co₃O₄ show decreased activity in D₂O compared to H₂O (Figure S13). The KIE values were calculated based on the current density in the protonic vs. deuterium solution at the same overpotential, exceeding 1.5 for both catalysts. This significant isotope effect indicates that proton transfer kinetics impose a substantial limitation on the RDS [52, 53]. Consequently, optimizing the local configuration of interfacial water is likely critical for lowering the energy barrier.

Therefore, we further investigated the interfacial water structure and dissociation dynamics to unravel the origin of the superior OER performance of RuO₂-Co₃O₄. The structure of interfacial water in the EDL within the range of 2800-3800 cm⁻¹ under different applied potentials was investigated using *in situ* ATR-SEIRAS. As shown in Figures 5a, 5b, and S14a, the broad band in the 2800-3800 cm⁻¹ region corresponds to OH stretching modes. To elucidate the influence of interfacial water on OER performance, the O-H stretching modes of interfacial water were analyzed using Gaussian fitting. The band can be deconvoluted into three distinct components: 4-HB-H₂O, 2-HB-H₂O, and free H₂O [32-38]. To gain deeper insight into the role of interfacial water molecular structure in acidic OER catalysis, the proportions of 4-HB-H₂O, 2-HB-H₂O, and free H₂O at different potentials were analyzed (Figures 5c, S14b, and S14c). Clearly, the proportion of free H₂O on RuO₂-Co₃O₄ is higher than that on Com-RuO₂ and Co₃O₄. Furthermore, as shown in Figure 5d, the interfacial free H₂O proportion on RuO₂-Co₃O₄ at different potentials is consistently greater than that on Com-RuO₂ and Co₃O₄ catalysts, indicating that enrichment of free H₂O at the catalyst surface is beneficial for improving acidic OER performance. Considering that interfacial water adsorption and subsequent dissociation pose a significant kinetic barrier for acidic OER, designing the interfacial water microenvironment in the EDL is crucial for enhancing electrochemical performance. To further verify this conclusion, the methanol oxidation reaction (MOR) was employed as a diagnostic probe to evaluate the adsorption behavior of surface *OH intermediates [54]. As shown in Figure 5e, RuO₂-Co₃O₄ displays a higher V_{OER}/V_{MOR} ratio compared to Com-RuO₂, indicating enhanced *OH intermediate capture [55, 56]. This is further supported by the larger MOR-OER current difference observed for RuO₂-Co₃O₄ (Figure S15), where stronger MOR competition directly reflects stronger surface *OH coverage from its faster H₂O transfer and

dissociation process.

Subsequently, *in situ* XAS measurements were employed to determine the chemical state and local coordination environment of Co under OER conditions. For both catalysts, the applied potential was sequentially stepped from open-circuit voltage (OCV) to 1.3 V and 1.5 V vs RHE, and then back to OCV in 0.5 M H₂SO₄ solution. As shown in Figure 5f and Figure S16, the absorption edge of Co₃O₄ shifts to higher values with increasing applied voltage, indicating its gradually increased oxidation state, consistent with previous reports in the literature [40, 57]. In contrast, the valence state of Co in RuO₂-Co₃O₄ slightly decreases with increasing applied bias, which demonstrates the electronic interaction between Co₃O₄ and RuO₂, activating the Ru sites during OER process. Moreover, the characteristic peaks of *in situ* EXAFS data for RuO₂-Co₃O₄ remains unchanged at different applied potentials, highlighting its high operating durability (Figure 5g). These results indicate that the construction of interfacial electric field effectively activates Ru sites and accelerates the water dissociation process during the OER process.

3.5 Theoretical calculations.

To further elucidate the origin of the enhanced OER performance, density functional theoretical (DFT) calculations were performed. Guided by the PXRD results and previous studies [9, 10, 40, 58], the RuO₂ (110) and Co₃O₄ (311) planes were chosen to construct the RuO₂-Co₃O₄ interface model. The geometric configurations on the calculated RuO₂-Co₃O₄ and RuO₂ were depicted in Figures 6a and S17. The charge density difference analysis of RuO₂-Co₃O₄ is visualized in Figure 6b. It is evident that there is an abundance of electrons at the Ru site and a deficiency at the Co site, which is in accordance with the aforementioned XPS conclusions, indicating that electrons transferred from RuO₂ to Co₃O₄ [59]. This electron transfer can be confirmed by the Bader charge analysis (Figure 6c), which reveals that negative charge is transferred from Ru to Co *via* the O bridge on the Ru-O-Co motifs, confirming that the heterostructure interface activates the Ru sites. Density of states (DOS) values for RuO₂-Co₃O₄ and RuO₂ were analyzed to investigate the hybridization between Ru 4d and O 2p orbitals. As shown in Figures 6d and 6e, upon the construction of the RuO₂-Co₃O₄ interface, the O 2p band center shifts away from the Fermi level compared with pristine RuO₂, inhibiting the lattice oxygen as a reactant [60]. Moreover, this core-shell structure enhances the d-p orbital hybridization between Ru and O (Figure 6f), thereby facilitating effective charge redistribution and adsorption optimization [61]. Guided by these findings, we constructed the corresponding adsorption models for RuO₂-Co₃O₄ and RuO₂ to evaluate the Gibbs free energy (Figure S18-S21). As shown in Figure 6g, for RuO₂-Co₃O₄, the potential-determining step of the AEM pathway requires a lower ΔG (1.84 eV) than that of the LOM pathway (2.16 eV). This lower value also explains its enhanced OER performance relative to pristine RuO₂, whose corresponding ΔG values are 2.07 eV for AEM and 1.86 eV for LOM.

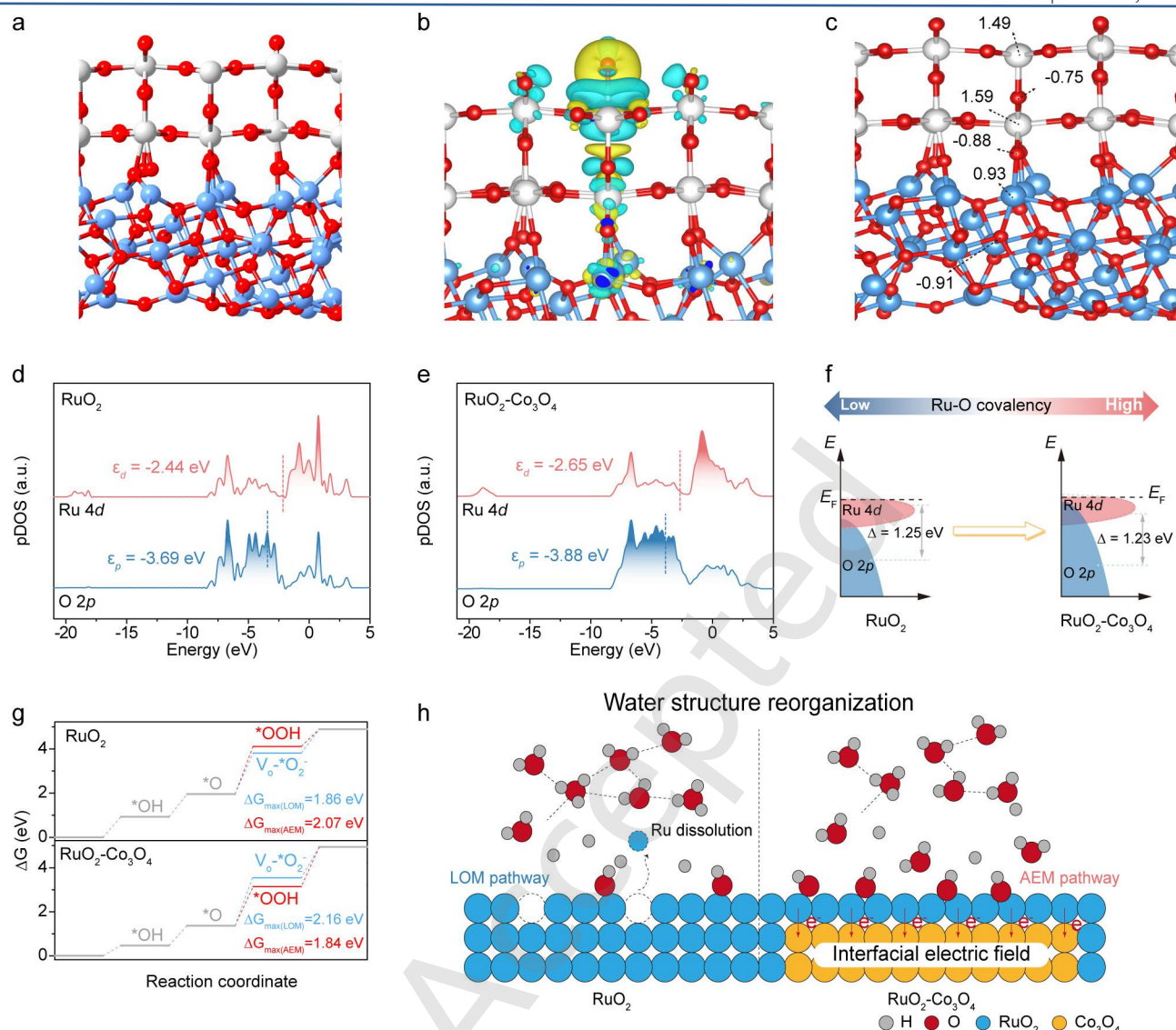


Figure 6 DFT theoretical analysis. (a) The geometric configuration on the calculated RuO₂-Co₃O₄ model. (b) Differential charge density distribution (sky blue regions represent the electron-deficiency and yellow regions represent the electron accumulation) in RuO₂-Co₃O₄. (c) The calculated Bader charge analysis for RuO₂-Co₃O₄ model. (d-e) DOS plots of Ru 4d and O 2p states for RuO₂ (d) and RuO₂-Co₃O₄ (e). (f) Schematic illustration of the Ru-O covalency regulation from RuO₂ to RuO₂-Co₃O₄. (g) Gibbs free energy illustration for RuO₂ and RuO₂-Co₃O₄ during OER by AEM or LOM pathways. (h) Schematic illustration of the interfacial electric field mediated reaction pathway transition and EDL optimization.

CONCLUSIONS

In summary, we have developed a core-shell RuO₂-Co₃O₄ catalyst that effectively addresses the dual challenges of ruthenium scarcity and instability in acidic OER. By integrating an ultrathin RuO₂ shell over Co₃O₄ nanocubes, this design maximizes ruthenium utilization efficiency while leveraging interfacial engineering to enhance durability. Comprehensive experimental and theoretical analysis reveals that the Co₃O₄ support dynamically modulates the electronic environment of Ru active sites, steering the reaction pathway toward the adsorbate evolution mechanism and suppressing lattice oxygen oxidation. Critically, the interfacial electric field disrupts the hydrogen-bonding network at the electrode-electrolyte interface, facilitating water dissociation and intermediate activation (Figure 6h). These synergistic effects yield a catalyst with a low overpotential of 222 mV at 10 mA cm⁻² and a high mass activity that is 27-fold greater than Com-RuO₂ at 1.54 V. When implemented in proton exchange membrane water electrolysis

with minimal ruthenium loading, the catalyst achieves satisfactory activity and stability, demonstrating its practical viability. This work highlights the pivotal role of interfacial electric fields and electronic modulation in designing high-performance, cost-effective electrocatalysts.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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calculations were performed on the supercomputing system at the National Supercomputing Center in Zhengzhou.

Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Yuelong Mao: Data curation, validation, writing manuscript, experimental design. Yang Xu: Data curation, validation. Ruirui Yu: Data curation, writing manuscript, experimental design. Suqian Liu: Data curation. Haijun Li: Writing manuscript. Shaomin Wang: Writing manuscript, experimental design. Hongnan Jia: Project administration, funding acquisition, writing manuscript, experimental design. Jingzhen Du: Project administration, funding acquisition, writing manuscript, experimental design. All the authors have approved the final manuscript.

Informed consent

Not applicable.

Ethics statement

Not applicable.

Use of AI statement

None.

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Electronic Supplementary Material

Interfacial electric field regulates surface water environment in RuO₂ coated Co₃O₄ for proton exchange membrane water electrolysis.

Yuelong Mao, Yang Xu, Ruirui Yu, Suqian Liu, Haijun Li, Shaomin Wang[✉], Hongnan Jia^{ID}[✉], and Jingzhen Du^{ID}[✉]

College of Chemistry, Zhengzhou University, Zhengzhou 450001, China

[✉]Address correspondence to Shaomin Wang, wshaomin@zzu.edu.cn; Hongnan Jia, hongnanjia@zzu.edu.cn; Jingzhen Du, jingzhendu@zzu.edu.cn

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Materials characterizations

The powder X-ray diffraction (PXRD) measurements were performed on a Miniflex 600 diffractometer (15 kV, 40 mA) with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Data were collected over a 2θ range of 10° to 80° at a scan rate of 3° min^{-1} . Transmission electron microscopy (TEM) imaging was conducted using a JEOL JEM-F200 microscope operating at 200 kV. For TEM sample preparation, a small amount of the catalyst was dispersed in 1 mL of anhydrous ethanol and ultrasonicated for 30 min. Subsequently, one drop of the resulting suspension was deposited onto an ultrathin carbon-film copper grid and dried at room temperature. The XPS measurements were conducted using a Thermo SCIENTIFIC K-ALPHA employing a monochromatic Al K α X-ray source. All the binding energies were calibrated with the characteristic C 1s peak at 284.8 eV. And the energy scales were calibrated with the Fermi level of the XPS instrument (4.57 eV vs. absolute vacuum value).

X-ray absorption fine structure (XAFS) spectroscopy was carried out using the Rapid XAFS 2 M (Anhui Absorption Spectroscopy Analysis Instrument Co., Ltd.) in transmission mode at 20 kV and 40 mA, and the Si (533) spherically bent crystal analyzer with a radius of curvature of 500 mm was used for Co. The obtained XAFS data were processed in Athena (version 0.9.26) for background, pre-edge line and post-edge line calibrations. Then Fourier-transformed fitting was carried out in Artemis (version 0.9.26). The k^2 weighting, k -range of $3\text{--}12 \text{ \AA}^{-1}$ and R range of $1\text{--}3.6 \text{ \AA}^{-1}$ were used for the fitting of RuO₂-Co₃O₄ and Co₃O₄; k -range of $3\text{--}12 \text{ \AA}^{-1}$ and R range of $1\text{--}3.6 \text{ \AA}^{-1}$ were used for the fitting of samples. The four parameters, coordination number, bond length, Debye-Waller factor and E_0 shift (CN, R , ΔE_0) were fitted without anyone was fixed, the σ^2 was set.

For the ¹⁸O isotope-labeled DEMS test, the QAS 100 mass spectrometer from Linglu Instruments in Shanghai was used. For the isotope labelling investigations, an electrolyte (0.5 M H₂SO₄) containing H₂¹⁸O was used to label the electrocatalyst at voltages from 0.9 to 1.6 V versus SCE. Then, the ¹⁸O-labelled electrocatalyst was subjected to multiple LSV cycles in an electrolyte (0.5 M H₂SO₄) with H₂¹⁶O as a solvent, and the gaseous products were detected by mass spectrometry.

In situ attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) was performed on a Bruker Invenio R spectrometer equipped with a liquid nitrogen-cooled detector. A custom-made cell with a polished Si prism was employed. The Si prism was sequentially ultrasonicated in acetone, ethanol, and ultrapure water, followed by chemical deposition of a thin Au layer to enhance conductivity and infrared signal sensitivity. Subsequently, 40 μL of catalyst slurry (5 mg/mL) was drop-cast onto the Au surface. The modified electrode was assembled in a three-electrode system using Hg/Hg₂Cl₂ (saturated KCl) as the reference electrode, a Pt plate as the counter electrode, and Ar-saturated 0.5 M H₂SO₄ as the OER electrolyte. All measurements were conducted via linear sweep voltammetry (LSV) at applied potentials of 1.2–1.8 V vs. RHE to probe OER intermediates and interfacial water behavior.

For *in situ* X-ray absorption spectroscopy (XAS) measurements, a custom-made Teflon cell with an X-ray transparent window was used, allowing X-rays to penetrate both the sample tape and electrolyte. The experiments were conducted using a three-electrode system, consistent with the electrochemical characterization conditions. XAS data were collected within the potential range of 1.3–1.5 V vs. RHE.

Preparation of working electrodes

For OER measurements, 3 mg RuO₂-Co₃O₄, 1 mg XC-72R and 0.6 mL 0.1 wt.% Nafion solution were ultrasonicated over 30 mins to obtain homogeneous ink. The glassy carbon electrode (GCE, 5 mm in diameter, 0.19625 cm² in disk area) was polished with 0.05 μm γ-Al₂O₃ powder, washed with absolute ethanol by sonication and dried under air to obtain a neat surface. Subsequently, 18 μL ink was dropped on the surface of the GCE (loading: ~0.45 mg cm_{geo}⁻²) and dried under air for further electrochemical tests.

Electrochemical characterizations

All electrochemical tests were performed on a CHI 760F electro-chemical workstation with a three-electrode system under O₂-saturated 0.5 M H₂SO₄ at 30 °C. The GCE loaded with catalysts was employed as the working electrode, the saturated calomel electrode (SCE, Hg/Hg₂Cl₂) was employed as a reference electrode and the graphite rod was employed as a counter electrode. In this work, all of the offered potentials were converted into the reversible hydrogen electrode (RHE) potential according to the following formula: E (vs. RHE) = E (vs. SCE) + 0.059*pH+ 0.242. Polarization curves were collected using a rotating disk electrode (RDE) with a rotation speed of 1600 rpm, with the potential scan range from 1.0 to 1.5 V (vs. SCE) under 0.5 M H₂SO₄. The chrono potentiometric stability tests were evaluated in 0.5M H₂SO₄ using a standard three-electrode system with carbon cloth. CV tests were carried out in the non-Faradaic region, employing a range of scan rates of 10, 20, 30, 40 and 50mV s⁻¹. The evaluation of ECSA was based on the C_{dl} value, which was obtained by plotting the Δj/2 (Δj = j_a - j_c, where j_a and j_c are anodic current and cathodic current, respectively at the middle potential) against the scan rate, where the slope is C_{dl} value. EIS measurements were performed with the AC impedance spectra at a frequency range of 100 kHz to 10 mHz with an amplitude of 5 mV.

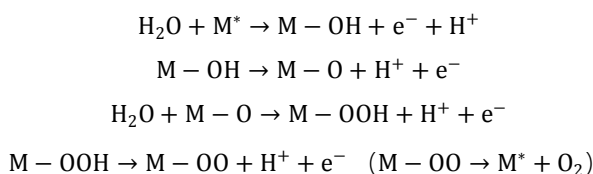
PEMWE electrolyser

Membrane electrode assemblies (MEAs) were fabricated utilizing a Nafion®115 polymer membrane (active area of 1 cm², film thickness: 127 μm). RuO₂-Co₃O₄ and commercial Pt/C catalysts were used as the anode and cathode, respectively. Electrochemical evaluation was carried out in proton exchange membrane water electrolysis (PEMWE). Pt-plated titanium felt was used as the anode gas diffusion layer (pressed against the RuO₂-Co₃O₄ catalyst side), and carbon paper was used as the cathode gas diffusion layer (pressed against the Pt/C catalyst side).

DFT calculations

All density functional theory (DFT) calculations were performed using the projected augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP 5.4.1). The electron interactions were described using the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional within the generalized gradient approximation (GGA) scheme. The cutoff energy was 400 eV and the self-consistent field (SCF) tolerance was 1×10⁻⁶ eV. The Brillouin zone was sampled by the Monkhorst-Pack scheme with a 4×4×1 k-points mesh for all of the surfaces. The (311) surface was selected to model Co₃O₄ phase and the (110) surface was selected to model RuO₂ phase. Then, the RuO₂-Co₃O₄ catalyst model was established based on these unit cells using VASP View 0.3.25. A 15 Å vacuum layer was added along the z-direction to eliminate periodic interactions. All atoms in the initial heterostructure were fully relaxed to achieve geometry optimization and energy convergence. During relaxation, the bottom atoms were fixed while the topmost two layers and the adsorbates were allowed to relax.

Accordingly, the Gibbs free energy changes for the water oxidation steps using AEM mechanism was calculated using the following Equations:



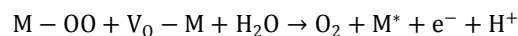
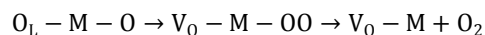
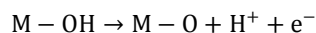
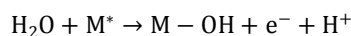
where * denotes adsorption active site on the substrate.

The Gibbs free energy of the adsorbed intermediate can be calculated as:

$$\Delta G = \Delta E_{ads} + \Delta E_{ZPE} - T\Delta S$$

where ΔE_{ads} is the DFT-computed adsorption energy, and ΔE_{ZPE} and $T\Delta S$ are the zero-point energy and entropy corrections, respectively.

The Gibbs free energy changes for the water oxidation steps using LOM mechanism was calculated using the following Equations:



It should be noted that we investigated the electrochemical processes by employing the established computational hydrogen electrode (CHE) model. The theoretical basis for the validity of the CHE model is that electrochemical reactions happened in the solution normally possess small kinetic barriers, which are surmountable at room temperature. The reaction kinetics thus be dictated by merely the free energy difference of each step. Therefore, the step with the most positive free energy difference is the rate-determining step. As a result, the theoretical overpotential η is defined in equation:

$$\eta_{theory} = \frac{\max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}}{e} - 1.23\text{V}$$

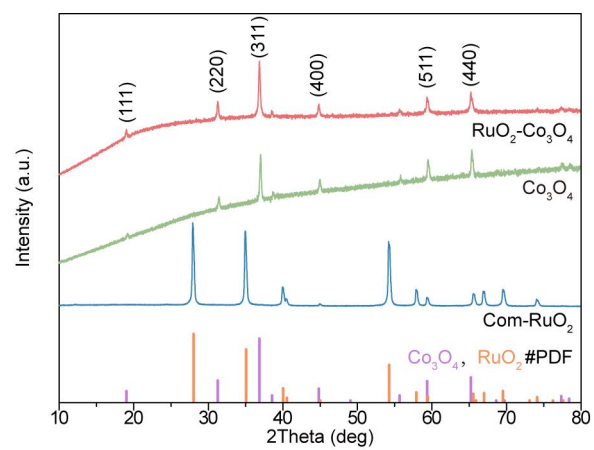


Figure S1. The PXRD pattern of Com-RuO_2 , Co_3O_4 and $\text{RuO}_2\text{-Co}_3\text{O}_4$.

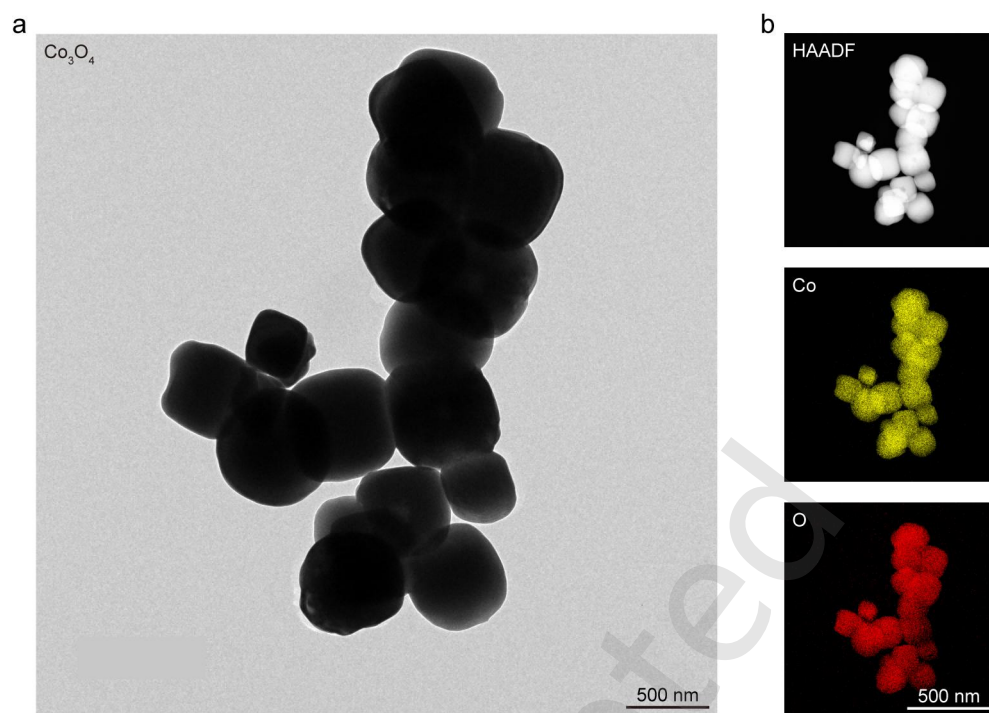


Figure S2. HRTEM image and corresponding elemental mapping of Co_3O_4 .

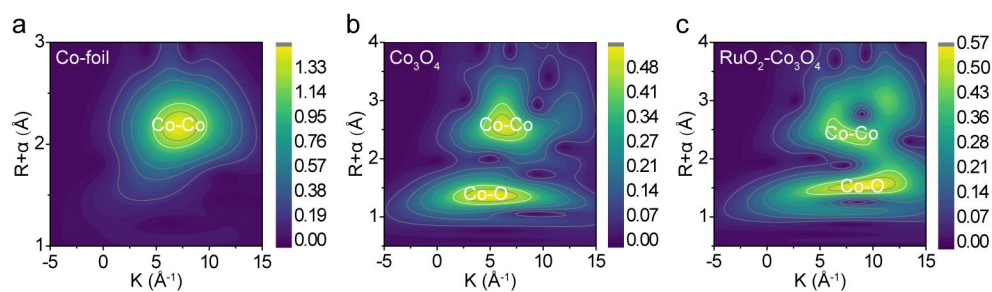


Figure S3. Wavelet transform of Co K-edge EXAFS data for Co-foil (a), Co_3O_4 (b) and $\text{RuO}_2\text{-Co}_3\text{O}_4$ (c).

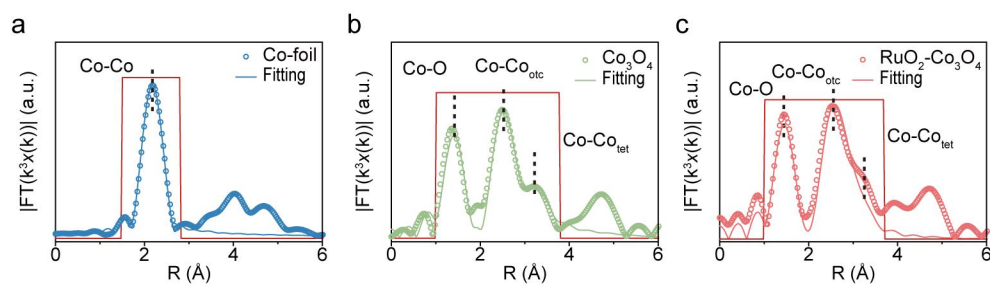


Figure S4. EXAFS fitting results of Co-foil (a), Co_3O_4 (b) and $\text{RuO}_2\text{-Co}_3\text{O}_4$ (c).

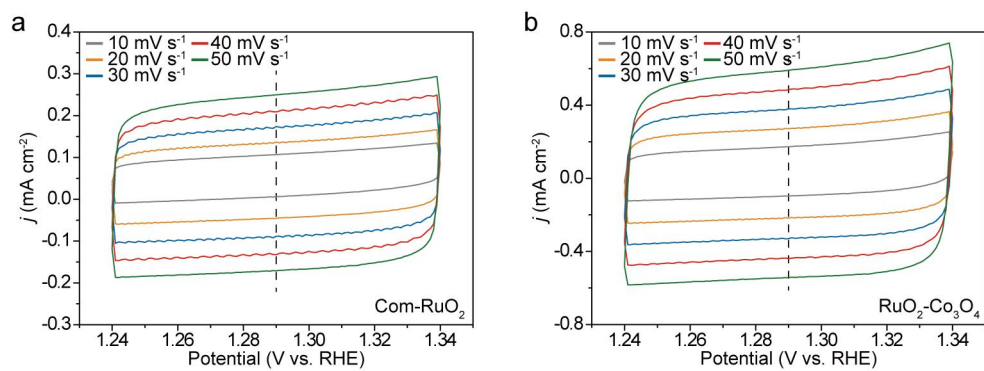


Figure S5. CV curves of Com-RuO₂ (a) and RuO₂-Co₃O₄ (b).

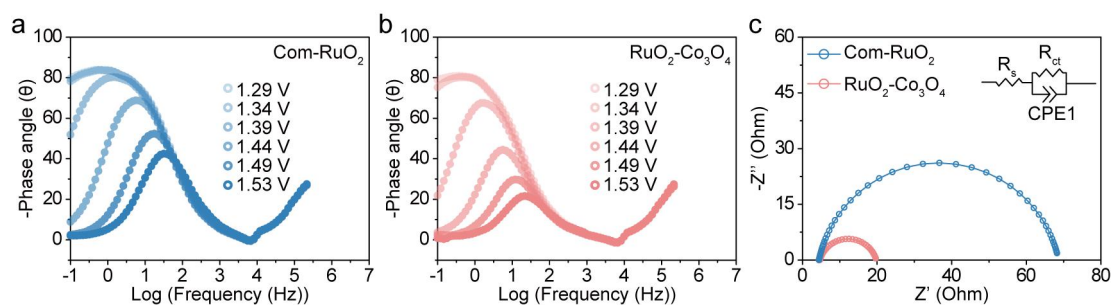


Figure S6. (a-b) Bode phase plots of Com-RuO₂ (a) and RuO₂-Co₃O₄ (b) at 1.29-1.53 V_{RHE}. (c) Electrochemical impedance spectroscopy of the Com-RuO₂ and RuO₂-Co₃O₄ at 1.49 V_{RHE}.

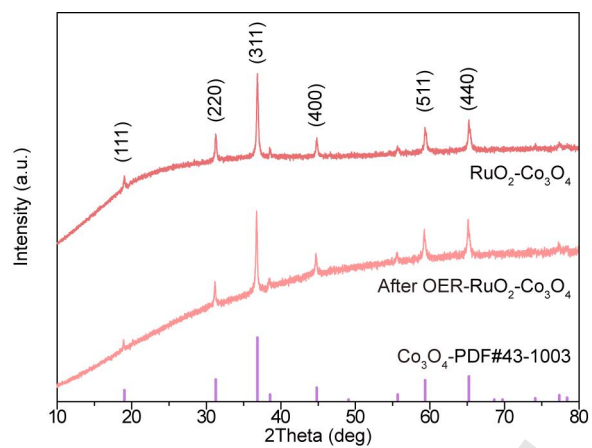


Figure S7. PXRD patterns of $\text{RuO}_2\text{-Co}_3\text{O}_4$ before and after OER in 0.5 M H_2SO_4 .

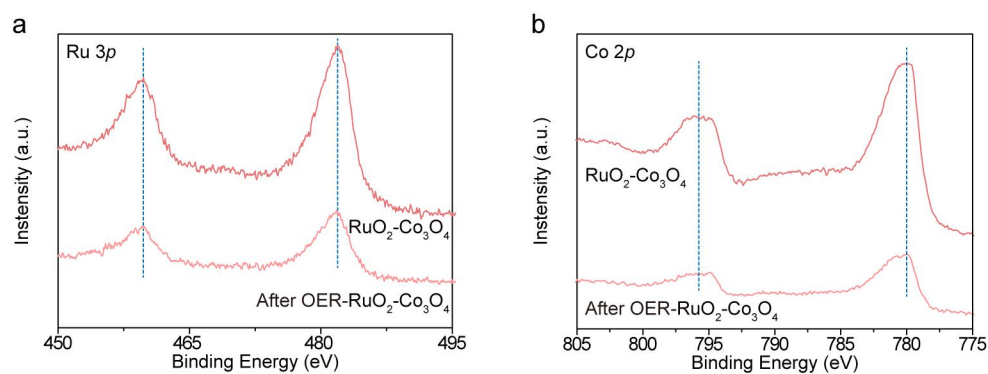


Figure S8. High resolution of Ru 3p and Co 2p XPS spectrum for RuO₂-Co₃O₄ before and after OER in 0.5 M H₂SO₄.

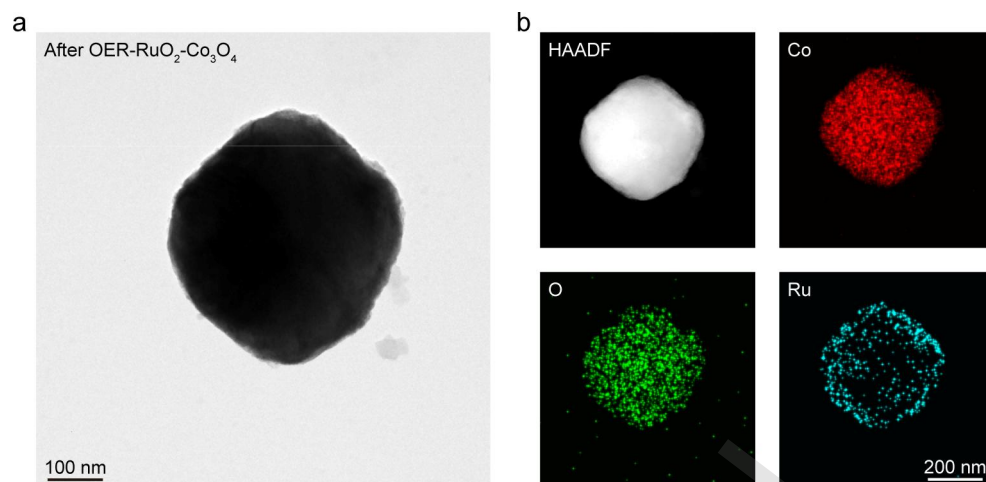


Figure S9 HRTEM image and corresponding elemental mapping of RuO₂-Co₃O₄ after OER in 0.5 M H₂SO₄.

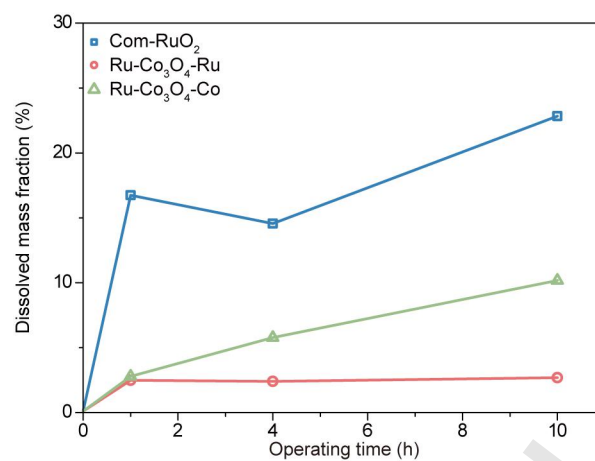


Figure S10. Dissolved mass fractions of Ru for Com-RuO₂, and Ru and Co for RuO₂-Co₃O₄ after operating times of 1, 4, and 10 h at 10 mA cm⁻² under 0.5 M H₂SO₄ electrolyte.

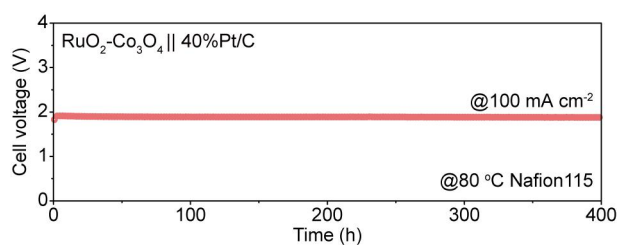


Figure S11. The chronopotentiometry stability test of RuO₂-Co₃O₄ at 100 mA cm⁻² in PEMWE.

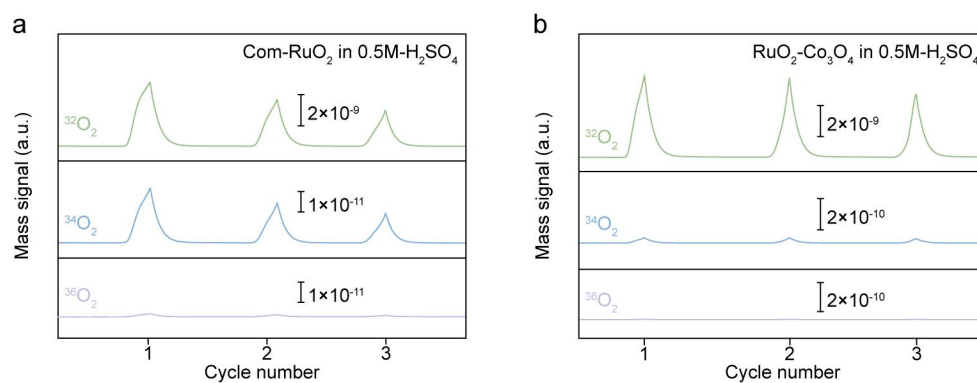


Figure S12. DEMS signals of O_2 products for ^{18}O labeled Com-RuO_2 (a) and $\text{RuO}_2\text{-Co}_3\text{O}_4$ (b) in $0.5\text{ M H}_2\text{SO}_4$ using H_2^{16}O as solvent during three consecutive LSV cycles (0.9-1.6 V vs. SCE, scan rate: 5 mV s^{-1}).

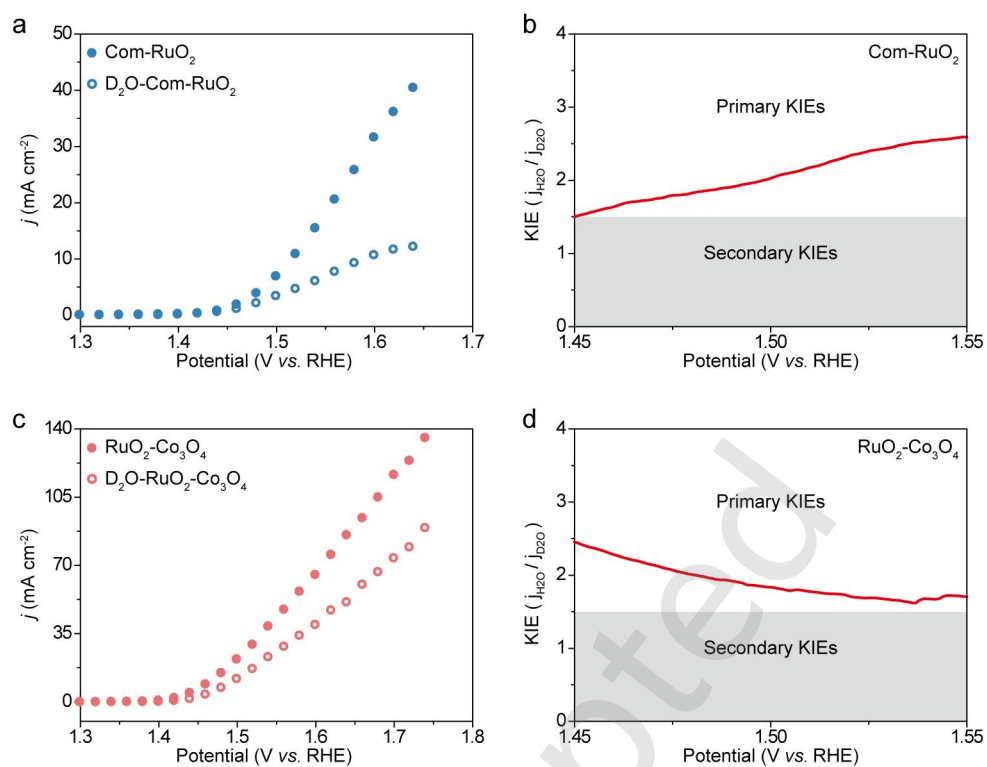


Figure S13. The kinetic isotope effects investigation by H/D isotope-labelled experiment. (a,c) Polarization curves of Com-RuO₂ and RuO₂-Co₃O₄ in 0.5 M H₂SO₄ dissolved in H₂O or D₂O without iR -compensation. (b,d) The corresponding KIE values at different overpotentials.

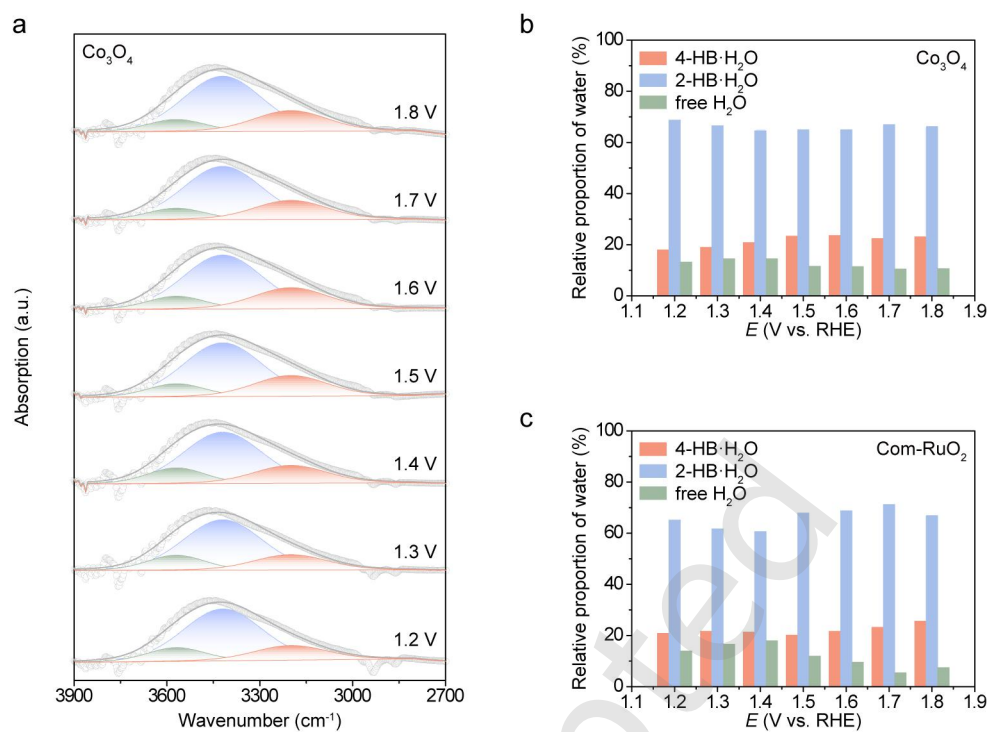


Figure S14. (a) Potential-dependent absorption strength of interfacial water through *in situ* ATR-SEIRAS in 0.5 M H_2SO_4 electrolyte for Co_3O_4 . (b, c) The relative proportion of 4-HB·H₂O, 2-HB·H₂O and free H₂O for Co_3O_4 (b) and Com-RuO₂ (c).

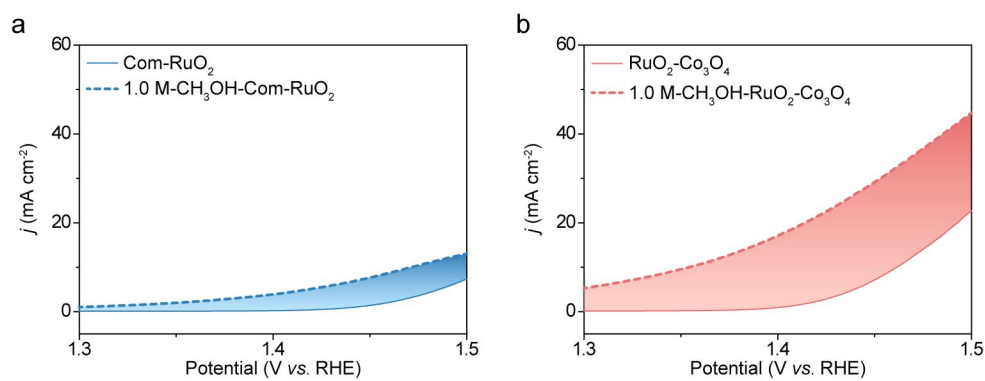


Figure S15. OER activity of Com-RuO₂ (a) and RuO₂-Co₃O₄ (b) in 0.5 M H₂SO₄ with or without methanol (1.0 M) solution.

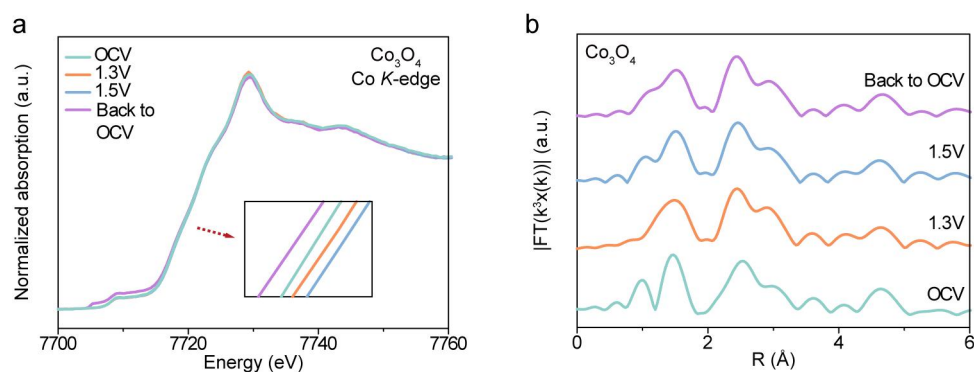


Figure S16. (a,b) *In situ* Co K-edge XANES (a) and corresponding EXAFS data (b) of Co_3O_4 , at OCV, 1.3 V_{RHE} , 1.5 V_{RHE} and Back to OCV, respectively.

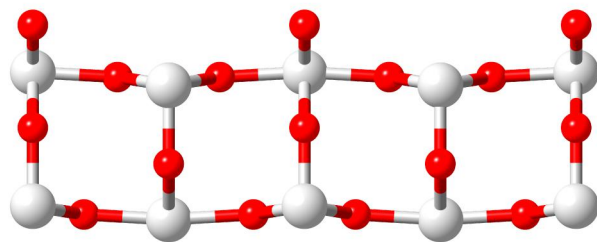


Figure S17. The geometric configuration of RuO₂. The light grey and red balls represent Ru and O atoms, respectively.

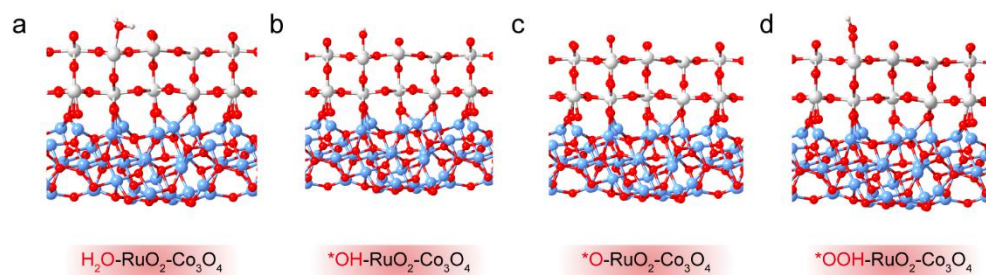


Figure S18. The geometric configuration of $\text{RuO}_2\text{-Co}_3\text{O}_4$ following AEM pathway. Different adsorbed species: (a), $^*\text{OH}_2$; (b) $^*\text{OH}$; (c) $^*\text{O}$; and (d) $^*\text{OOH}$ on Ru site. The light grey, light pink, bright blue, and red balls represent Ru, H, Co and O atoms, respectively.

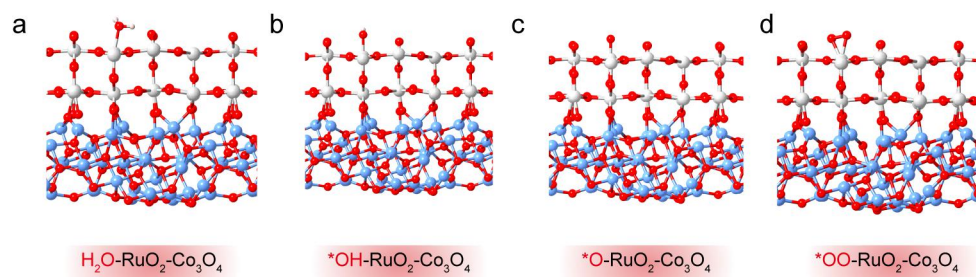


Figure S19. The geometric configuration of $\text{RuO}_2\text{-Co}_3\text{O}_4$ following LOM pathway. Different adsorbed species: (a), $^*\text{OH}_2$; (b) $^*\text{OH}$; (c) $^*\text{O}$; and (d) $^*\text{OO}_v$ on Ru site. The light grey, light pink, bright blue, and red balls represent Ru, H, Co and O atoms, respectively.

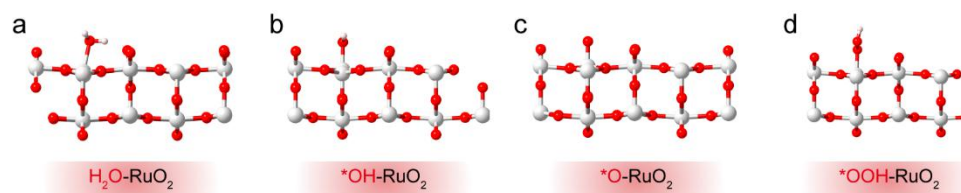


Figure S20. The geometric configuration of RuO₂ following AEM pathway. Different adsorbed species: (a), *OH₂; (b) *OH; (c) *O; and (d) *OOH on Ru site. The light grey, light pink and red balls represent Ru, H and O atoms, respectively.

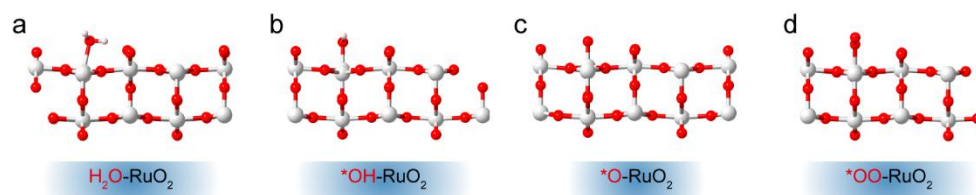


Figure S21. The geometric configuration of RuO₂ following LOM pathway. Different adsorbed species: (a), *OH₂; (b) *OH; (c) *O; and (d) *OO on Ru site. The light grey, light pink and red balls represent Ru, H and O atoms, respectively.

Table S1. Metal atomic composition determined by ICP-OES

Sample	Atomic ratio of Co	Atomic ratio of Ru
RuO₂-Co₃O₄	97.9%	2.1%

Just Accepted

Table S2. Structural parameters extracted from the Co K-edge EXAFS fitting ($S_0^2 = 0.69$).

Sample	Scattering pair	CN	R (Å)	ΔE_0 (eV)	$\sigma^2 (10^{-3} \text{ Å}^2)$	R factor
Co foil	Co–Co	12	2.50	6.76	6	0.002
	Co–O	5.12±0.51	1.90	0.75	6	
Co ₃ O ₄	Co–Co	5.75±0.60	2.90	9.19	5	0.018
	Co–Co	4.28±0.75	3.45	9.19	3	
RuO ₂ -Co ₃ O ₄	Co–O	3.42±0.34	1.92	4.52	3	
	Co–Co	3.21±0.63	2.87	3.70	3	0.020
	Co–Co	5.45±1.14	3.37	3.70	6	

For the EXAFS fitting, S_0^2 is the amplitude reduction factor; CN is the coordination number; R is interatomic distance (the bond length between Co central atoms and surrounding coordination oxygen atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatter distances); ΔE_0 is edge energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.

Table S3 R_s and R_{ct} of different electrocatalysts at 1.49 V_{RHE}.

sample	$R_s(\Omega)$	$R_{ct}(\Omega)$
Com-RuO ₂	4.43	64.25
RuO ₂ -Co ₃ O ₄	4.71	15.12

Just Accepted

Table S4 Comparison of overpotentials and stability for RuO₂-Co₃O₄ with other reported Ru-based OER catalysts.

Catalyst	Structural configuration	Atomic ratio of Ru	Overpotential @10 mA cm ⁻²	PEM durability	Mass activity	Reference
RuO ₂ -Co ₃ O ₄	Core-shell structure	2.1 %	222 mV	400 h	376.6 A g ⁻¹ @1.54 V _{RHE}	This work
Co ₃ O ₄ @RuO ₂	Core-shell structure	N.R.	189 mV	400 h	N.R.	<i>Adv. Energy Mater.</i> 2025 , 15, 2502367.
Ru/RuO ₂ -Co ₃ O ₄	Oxygen-vacancy-heterostructure	20.2 %	226 mV	N.R.	N.R.	<i>ACS Sustainable Chem. Eng.</i> 2023 , 11, 5155-5163.
8-Ru-Co ₃ O ₄ /Ti	Sub-nanocluster heterostructure	N.R.	165 mV	N.R.	N.R.	<i>InfoMat.</i> 2025 , 7, e70003.
RuCo	Alloy nanoparticles	N.R.	210 mV	N.R.	N.R.	<i>Adv. Funct. Mater.</i> 2025 , 35, e09656.
RuO ₂ /Ni-Co ₃ O ₄	Inter-doped-heterostructure	2.7 %	186 mV	N.R.	1202.3 A g ⁻¹ (@η=250 mV)	<i>J. Colloid Interface Sci.</i> 2025 , 682, 548.
Cr-MnO ₂ /RuO ₂	Heterostructure	23.9 %	193 mV	1168 h	406 A g ⁻¹ (@η=270 mV)	<i>Adv. Funct. Mater.</i> 2026 , 36, e77098.
ZrO ₂ -5.5RuO ₂	Heterostructure	65 %	137 mV	N.R.	337.5 A g ⁻¹ (@η=250 mV)	<i>Adv. Mater.</i> 2026 , 38, e22946.
Mn _{0.2} RuO ₂	Doped	83.3 %	188 mV	180 h	47.7 A g ⁻¹ (@η=188 mV)	<i>Nat. Commun.</i> 2024 , 15, 8089.
CA-RuO _x	Crystalline-amorphous	N.R.	194 mV	50 h	263 A g ⁻¹ @1.5 V _{RHE}	<i>Sci.</i> 2026 , 717, 140452.
H ₁₀₀₀ -RuIr-Mo/WVOx	Heterostructure	27 %	183 mV	N.R.	210.7 A g ⁻¹ @1.49 V _{RHE}	<i>Adv. Mater.</i> , 2026 , 38, e73229.
RuTiO _x @TM	Doped	N.R.	248 mV	200 h	132 A g ⁻¹ @1.53 V _{RHE}	<i>Sci. Bull.</i> , 2026 , 71, 2811.