Interface engineering breaks both stability and activity limits of RuO$_2$ for sustainable water oxidation

Designing catalytic materials with enhanced stability and activity is crucial for sustainable electrochemical energy technologies. RuO$_2$ is the most active material for oxygen evolution reaction (OER) in electrolyzers aiming at producing ‘green’ hydrogen, however it encounters critical electrochemical oxidation and dissolution issues during reaction. It remains a grand challenge to achieve stable and active RuO$_2$ electrocatalyst as the current strategies usually enhance one of the two properties at the expense of the other. Here, we report breaking the stability and activity limits of RuO$_2$ in neutral and alkaline environments by constructing a RuO$_2$/CoO$_x$ interface. We demonstrate that RuO$_2$ can be greatly stabilized on the CoO$_x$ substrate to exceed the Pourbaix stability limit of bulk RuO$_2$. This is realized by the preferential oxidation of CoO$_x$ during OER and the electron gain of RuO$_2$ through the interface. Besides, a highly active Ru/Co dual-atom site can be generated around the RuO$_2$/CoO$_x$ interface to synergistically adsorb the oxygen intermediates, leading to a favourable reaction path. The as-designed RuO$_2$/CoO$_x$ catalyst provides an avenue to achieve stable and active materials for sustainable electrochemical energy technologies.

The practical application of water electrolyser in the generation of sustainable green hydrogen energy$^{1-3}$ calls for the development of stable and active electrocatalysts. So far, RuO$_2$ is the most active electrocatalyst for anodic oxygen evolution reaction (OER) in water electrolysis$^{4-9}$. Unfortunately, as indicated by Pourbaix diagram$^{10-12}$, RuO$_2$ is thermodynamically unstable under OER conditions over the entire pH range. This has been verified by extensive theoretical and experimental investigations$^{4,13-15}$, which demonstrate that the proceeding of OER is accompanied by the transformation of stable Ru$^{4+}$ to unstable Ru$^{3+}$, resulting in the gradual dissolution and deactivation of the catalyst. Common strategies of improving the stability of RuO$_2$ include mixing RuO$_2$ with a more corrosion resistant material in the synthetic procedure$^{16-20}$, and controlling the dispersion of RuO$_2$ to avoid direct contact with the electrolyte$^{21}$. In these cases, however, the stability of Ru-based catalysts is generally enhanced at the expense of its activity, leading to a seesaw relation between stability and activity$^{14,21-26}$. It is necessary to develop new strategy to achieve both enhanced stability and activity for Ru-based catalysts.

To substantially enhance the stability of RuO$_2$ catalysts under OER conditions, we identify that the key is to suppress the electrochemical corrosion of Ru species. There is a classic fashion of using a sacrifice component to protect the target material. For example, in the well-known zinc-plated steel$^{27}$, the more reactive zinc is preferentially oxidized to form a dense oxide film over the steel, preventing the further...
oxidation of zinc and the corrosion of steel. Inspired by this, we assumed that implementing a proper material with RuO₂ to form a stable interface can be a promising strategy to stabilize RuO₂ catalyst. On the other hand, previous works of Nørskov et al. have suggested that the ‘stable’ RuO₂ exhibits unsatisfactory catalytic activity due to the lack of unstable high-valence Ru⁶⁺⁺ species. Regarding this, the construction of an interface may create new active sites to break the activity limit of ‘stable’ RuO₂. Moreover, the interface construction may use some cost-effective materials to reduce the use of precious metal Ru and achieve sustainable water electrolysis.

Herein, we report constructing a RuO₂/CoOₓ hybrid catalyst to break the stability-activity seesaw relation on RuO₂ catalyst. Combining theoretical calculations, in situ X-ray photoelectron spectroscopy (XPS) with in situ UV-visible (UV-Vis) absorption spectroscopy, we demonstrate that the stability of the new RuO₂/CoOₓ hybrid significantly exceeds the Pourbaix limits of bulk RuO₂. This is ascribed to the sacrificing oxidation of CoOₓ and interfacial electronic effects, which stabilized RuO₂ by decreasing driving force for RuO₂ dissolution and enriching electrons on RuO₂. In addition, as verified by kinetic isotope effect (KIE), in situ infrared reflection (IR) measurements and theoretical calculations, the construction of interface creates highly active Ru/Co dual-atom sites around the RuO₂/CoOₓ interface, which synergistically absorb the key oxygen intermediates during OER to optimize the reaction thermodynamics and kinetics. Therefore, the RuO₂/CoOₓ catalyst achieves superior high OER activities under neutral and alkaline conditions accompanied by excellent long-term stability.

**Results**

**Stabilization of RuO₂ on CoOₓ support**

According to our calculated Pourbaix diagram of RuO₂ (Fig. 1a), RuO₂ undergoes oxidation in the OER potential range, forming high-valence Ru⁶⁺⁺ ions that dissolve in the electrolyte. We assume that depositing RuO₂ on an appropriate support that can be preferentially oxidized represents a rational strategy to protect RuO₂ from dissolution in harsh electrochemical oxidation. To test this hypothesis, CoOₓ was selected as the support material, which is easily oxidized under the anodic potential in the OER range (Supplementary Fig. 1). The calculated Pourbaix diagram of RuO₂/CoOₓ (Supplementary Note 1) in near-neutral and alkaline environments is shown in Fig. 1b. As expected, the CoOₓ support is gradually oxidized from CoO to CoO₂, CoOOH and eventually CoO₂ with the increase of anodic potential. Hereafter, CoOₓ repents these cobalt oxides for simplicity. Significantly, RuO₂ can construct stable interfaces with the oxidation products of CoOₓ (CoO, CoO₂, CoOOH, and CoO₂) within the entire OER potential range (Fig. 1b, c). Besides, stable Ru–O–Co chemical bond can be formed at the RuO₂/CoOₓ interface (Fig. 1c and Supplementary Fig. 2), which enables the hybrid to gain considerable energy from constructing the interface (Supplementary Fig. 2). This undoubtedly lowers the energy of the hybrid system and decreases the driving force for RuO₂ dissolution, thus stabilizing RuO₂ in the hybrid catalyst.

To further understand the interfacial effect on stabilizing RuO₂, Bader charge analysis was performed on four RuO₂/CoOₓ catalysts, i.e., RuO₂/CoO, RuO₂/CoO₂, RuO₂/CoOOH, and RuO₂/CoO₂. As shown in Fig. 1d–f, the changes in the charges of Ru, O and Co ions at the interface relative to those in their corresponding bulk materials show a similar trend among the four catalysts. Taking RuO₂/CoOOH as an example, the average charge of Ru ions away from the interface in RuO₂ is ~6.3 e⁻, which increases to 6.7 e⁻ at the interface (Fig. 1d), indicating the enrichment of electrons on the interfacial Ru ions. Similarly, the average charge of O ions in the bulk RuO₂ is ~6.6 e⁻, which increases to ~6.7 e⁻ at the interface, and further increases to ~7.0 e⁻ in the bulk CoOOH (Fig. 1e). Note that the Co charge at the support...
interface is almost identical to that in the bulk CoOOH (Fig. 1f). These results indicate that O ions in the hybrids play a key role in the electron enrichment in interfacial Ru ions. This is due to the different metal-oxygen hybridizations in RuO$_2$ and CoOOH, resulting in different O charges in these two materials. That is, the O ions connecting with Co ions own more electrons compared with those connecting with Ru ions. Once Ru–O–Co bond is formed at the RuO$_2$/CoO$_x$ interface, the electron-rich O ions connecting with Co ions contribute electrons to the nearby Ru ions through metal-oxygen re-hybridization, thus enriching electrons in the interfacial Ru ions.

**Synthesis of RuO$_2$/CoO$_x$ hybrid catalyst**

Guided by the above theoretical findings, RuO$_2$/CoO$_x$ hybrid catalyst was fabricated by depositing Ru nanoparticles on CoO nanorods (Fig. 2a), followed by an electrochemical oxidation process (Supplementary Figs. 3–8). As shown in Fig. 2b, c, the CoO nanorods possess faceted surface with prefabricated nanoscale roughness to uniformly load Ru nanoparticles. The Ru nanoparticles form a fish scale-like single-layer with a thickness of 2 nm on the surface of CoO nanorods (Supplementary Fig. 5). Subsequent electrochemical oxidation resulted in in situ conversion of Ru to RuO$_2$ on CoO$_x$ nanorods (Supplementary Figs. 7 and 8). This method features the epitaxial growth of RuO$_2$ on CoO$_x$ nanorods (Fig. 2d), providing a structural basis for strong interfacial geometric and electronic interaction between RuO$_2$ and CoO$_x$. The as-formed interface was closely inspected by sub-Ångstrom resolution aberration corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Fig. 2d and Supplementary Fig. 9), showing an atomic-level tight connection of Ru, O and Co atoms at the interface. This finding was supported by the Fourier transform extended X-ray absorption fine structure (FT-EXAFS) of RuO$_2$/CoO$_x$ (Supplementary Fig. 10).

Electron energy-loss spectroscopy (EELS) at Ru-M$_{2,3}$, O-K, and Co-L$_{2,3}$ absorption edges was performed to investigate charge changes of Ru, O and Co ions across the interface (from point 1 to point 5) in Fig. 2d. As illustrated in Fig. 2e, the collected Ru-M$_{2,3}$ spectrum at the interface (point 3) shifts 0.3 eV toward the low energy loss direction with respective to that of RuO$_2$ (point 1), indicating a decreased Ru valence at the interface. For O-K edge spectra (Fig. 2f), the curves show obvious shape change from RuO$_2$-like (point 1) to CoO$_x$-like (point 5). In particular, the characteristic peak ‘a’ collected in CoO$_x$ gradually weakens towards the interface until disappears in RuO$_2$. This reflects different electronic properties of O atoms connecting with Ru and Co atoms, respectively, and re-hybridization of O atoms at the interface caused by simultaneous connection with Ru and Co atoms. Notably, no noticeable peak shift is observed in the collected Co-L$_{2,3}$ spectra (Fig. 2g and Supplementary Fig. 11). These experimental results well support the calculated evident charge change of O ions from CoO$_x$ to RuO$_2$ via the interface (Fig. 1e), while no significant O charge change from bulk CoO$_x$ to the interface (Fig. 1f). This indicates that O ions play a decisive role in the reduction of Ru valence through the electronic interaction among Ru, O and Co atoms at the interface. We note that the enrichment of Ru charge at the interface will affect the distribution of Ru charge in the bulk and on the surface through continuous Ru–O bonds.

![Fig. 2 | Synthesis of RuO$_2$/CoO$_x$ hybrid catalyst.](image-url)
Stability evaluation of RuO$_2$/CoO$_x$ hybrid catalyst during OER. Afterwards, the stability of RuO$_2$/CoO$_x$ hybrid catalyst during OER in neutral environment was monitored by in situ XPS (Supplementary Figs. 12 and 13). Significantly, the Ru $3d$ XPS peak at 280.9 eV exhibits negligible changes with the applied potential increased from 1.0 to 2.0 V versus reversible hydrogen electrode (RHE) (Fig. 3a). Detailed quantitative analysis shows the co-existence of Ru$^{3+}$ and Ru$^{4+}$ species with almost identical percentages from 1.0 to 2.0 VRHE (Fig. 3b and Supplementary Fig. 14). Surprisingly, even at 2.0 VRHE, there is still 9% of Ru$^{3+}$ remaining in the RuO$_2$/CoO$_x$ hybrid. Considering that the average particle size of RuO$_2$ is ~2 nm, the theoretical proportion of interfacial Ru atoms to total Ru atoms should be about 15% (Supplementary Note 2 and Supplementary Fig. 15). This value is in agreement with the percentage of Ru$^{3+}$ species as demonstrated by the in situ XPS results (Fig. 3b), indicating the critical role of the constructed interface in stabilizing RuO$_2$ in the hybrid.

Moreover, although the Ru valence state of RuO$_2$/CoO$_x$ hybrid did not exceed 4+ in the studied potential range, the Co valence state increased significantly during OER as evidenced by in situ UV–Vis spectroscopy characterization and quantitative electron paramagnetic resonance (EPR) analysis. It was demonstrated that as the anodic potential increased, the Co ions in the hybrid catalyst underwent gradual oxidation from Co$^{2+}$ to Co$^{3+}$ and Co$^{4+}$ without dissolution (Fig. 3c, d, Supplementary Fig. 16 and Supplementary Table 1). This is consistent with the calculated Pourbaix diagram of the hybrid catalyst (Fig. 1b) and verified our hypothesis that the support CoO$_x$ was preferentially oxidized to protect RuO$_2$.

The above in situ spectroscopic results were supported by the experimentally observed remarkable stability of RuO$_2$/CoO$_x$ during OER. As shown in Fig. 3e, Supplementary Figs. 17 and 18 and Supplementary Table 1, after 20 h continuous stability test at the potential as high as 1.80 VRHE, the content of Ru element in the hybrid catalyst was still close to 100%. Significantly, the RuO$_2$/CoO$_x$ catalyst works stably at a constant current density of 10 mA cm$^{-2}$ for more than 200 h (Fig. 3f), and affords an excellent dynamic stability with varied current density from 10 to 100 mA cm$^{-2}$ (Supplementary Fig. 19).
pristine RuO₂ (deposited on carbon black, Supplementary Figs. 20 and 21) encountered severe catalyst dissolution and performance degradation (Fig. 3f and Supplementary Fig. 22), which agrees well with the literature. Additionally, the RuO₂/CoOₓ also demonstrated excellent stability in alkaline environment (Supplementary Figs. 23, 24 and Supplementary Table 2).

**OER activity and rate-determining step of RuO₂/CoOₓ.**

Under the incentive of the high stability, we evaluated the OER activity of the RuO₂/CoOₓ hybrid catalyst with a RuO₂ mass loading of 10 µg on per cm² electrode (Supplementary Table 3, Supplementary Figs. 25 and 26). Note that RuO₂ (Supplementary Fig. 27 and Supplementary Table 4) and CoOₓ catalysts were measured as control samples. As shown in Fig. 4a and Supplementary Fig. 28, the RuO₂/CoOₓ exhibits a much higher OER activity than RuO₂ and CoOₓ in neutral electrolyte, affording an ultra-low overpotential of 0.24 V to drive an OER current density of 10 mA cm⁻² at 1200 V RHE. Besides, the current density of RuO₂/CoOₓ can achieve 400 mA cm⁻² at 1.92 V as the mass of RuO₂/CoOₓ catalyst is increased to 1.5 mg cm⁻² on nickel foam (Supplementary Fig. 29). Impressively, the RuO₂/CoOₓ is amongst the most active OER catalysts reported so far under neutral conditions (Supplementary Table 3). Moreover, the turnover frequency (TOF) of the RuO₂/CoOₓ was estimated by normalizing the O₂ generation rate to the total number of Ru ions on CoOₓ support (Supplementary Note 3). At an overpotential of 400 mV, the RuO₂/CoOₓ delivers a high TOF of 3.61 s⁻¹, representing a 10-time enhancement in comparison with the optimum value reported previously on Ru-based catalysts (RuIrCaOₓ, 0.36 s⁻¹). Moreover, the RuO₂/CoOₓ achieves a high OER Faradaic efficiency of ~98% at 10 mA cm⁻² (Supplementary Fig. 30).

To reveal the activity origin of the RuO₂/CoOₓ, we explored the rate-determining step (RDS) of OER by Tafel plots. As illustrated in Fig. 4b, the RuO₂/CoOₓ shows a significantly decreased Tafel slope (70 mV dec⁻¹) compared with the RuO₂ (109 mV dec⁻¹), indicating the possible different RDSs in these two catalysts. The O¹⁸/O¹⁶ isotope effect was then employed in both catalysts to probe the O–O bond formation, which is generally considered as the RDS in OER. As shown in
Fig. 4c, there is an obvious decrease in the OER current density on the RuO$_2$ catalyst when the electrolyte was changed from H$_2$O to H$_2$O$_{18}$, and the KIE value of the O–O bond formation step (KIE$_{O-O}$) is estimated as 1.03 (Supplementary Fig. 31). Since the KIE$_{O-O}$ value falls within the range between 1.01 and 1.04,$^{34,35}$ the O–O bond formation step can be confirmed to be the RDS of the RuO$_2$. In contrast, the negligible ΔJ between H$_2$O and H$_2$O$_{18}$ on the RuO$_2$/CoO$_x$ demonstrates that O–O bond formation is not the RDS (Fig. 4d). This finding is further supported by the in situ IR spectroscopy characterization (Fig. 4e, Supplementary Fig. 32 and Supplementary Table 6), which shows a more pronounced *OOH band of RuO$_2$/CoO$_x$ in comparison with that of RuO$_2$ (Fig. 4f). These results suggest that the RuO$_2$/CoO$_x$ exhibits a different RDS compared with the pristine RuO$_2$ as we will discuss in detail later.

Furthermore, we demonstrate that the RuO$_2$/CoO$_x$ hybrid catalyst delivers a superior high OER performance in alkaline environment, permitting it a promising candidate for highly efficient OER electrocatalysts in a wide pH range (Supplementary Fig. 33 and Supplementary Table 7).

**Origin of enhanced OER activity on RuO$_2$/CoO$_x$**

A key question remains how the RuO$_2$/CoO$_x$ interface significantly boosts the OER activity of RuO$_2$. To shed light on this, density functional theory (DFT) calculations were performed. In particular, HADDF-STEM imaging (Fig. 5a) shows that Ru/Co dual-atom sites were exposed around the RuO$_2$/CoO$_x$ interface after treating the hybrid at the OER onset potential (~1.40 V$_{RHE}$). Accordingly, the computational model was constructed (Fig. 5b). It was found that the exposed Ru/Co dual-atom site around the interface is the most active site for OER (Supplementary Figs. 34–36); the oxygen intermediates, i.e., *OH, *O and *OOH, tend to be co-adsorbed at the Ru/Co dual-atom site to form a stable nearly quadrilateral structure (Fig. 5c, inset). Significantly, the triatomic *OOH bends downward and the H atom forms a hydrogen bond with the surface O in the CoO$_x$ to construct a unique *OOH/Co$_x$H$_2$ adsorption configuration. Due to the electrostatic attraction of O atom in the CoO$_x$, the O–H bond length in the formed *OOH increases compared with that on the pristine RuO$_2$ (Supplementary Fig. 35). According to previous work,$^{36}$ when the intramolecular hydrogen bond stretches the bond in the probe molecule, it will lead to a shift of the stretching vibrational frequency of the probe groups toward the low wavenumber direction in IR spectra. Relative shift of *OOH bands is observed in the in situ IR spectra of the RuO$_2$/CoO$_x$ compared with those of RuO$_2$ (Fig. 4e, f), verifying the adsorption configuration of *OOH at the Ru/Co dual-atom site around the interface (inset of Fig. 5c).

Note that *OOH is a key intermediate during OER, which exhibits a high formation barrier and restricts the OER activity of catalysts.$^{32,33}$ The calculated Gibbs free energy for *OOH formation (Δ$G_{OOH}$) on the RuO$_2$...
is as high as 1.12 eV (Fig. 5c and Supplementary Fig. 35). Notably, this calculated value of $\Delta G_{\text{OHR}}$ is consistent with the result reported by Nørskov et al. and other researchers, indicating an inferior OER activity of 'stable' RuO$_2$ with the absence of the generated high-valent Ru$^{IV}$ species during OER. As expected, for the RuO$_2$/CoO$_x$, the *OOH formation is greatly facilitated at the Ru/Co dual-atom site around the interface. More importantly, this shifts the RDS of RuO$_2$/CoO$_x$ to the subsequent step of *OOH formation – that is, desorption of *O$_2$ (Supplementary Note 4), which demonstrates a significantly decreased energy injection of 0.50 eV (Fig. 5c). This exciting finding agrees well with the KIE and in situ IR results (Fig. 5c–f). Therefore, our self-consistent experiments and calculations confirm that the artificially constructed RuO$_2$/CoO$_x$ hybrid catalyst successfully breaks the OER activity limit of 'stable' RuO$_2$ by changing the RDS of OER through exposing the highly active Ru/Co dual-atom sites around the RuO$_2$/CoO$_x$ interface (Supplementary Note 5 and Supplementary Figs. 37–39).

**Discussion**

In summary, we constructed the RuO$_2$/CoO$_x$ hybrid catalyst to break the stability and activity limits of RuO$_2$ by decoupling its stability–activity relation. Specifically, the sacrificial oxidation of CoO$_x$ and the electron interaction among the face-to-face Ru–O–Co interfacial atoms enhance the stability, while the Ru/Co dual-atom site exposed around the interface is responsible for the improved activity. With such unique electronic and geometric effects generated by the RuO$_2$/CoO$_x$ interface, we solved the critical issues of RuO$_2$ under OER conditions and achieved high stability and excellent activity. Our work provides an atomic scale understanding of employing interfacial effects such as interfacial electronic and geometric effects generated by the RuO$_2$/CoO$_x$ interface to simultaneously enhance the stability and activity of RuO$_2$. We believe that under the guideline built by the RuO$_2$/CoO$_x$ interface, the activity and stability issues of RuO$_2$ in acidic environments can also be fundamentally solved by selecting appropriate support materials. We expect that this work will also contribute to future research on other renewable energy technologies coupled with OER in neutral environments, such as reduction of carbon dioxide to multi-carbon fuels.

**Methods**

**Synthesis of RuO$_2$/CoO$_x$ and RuO$_2$ catalysts**

RuO$_2$/CoO$_x$ catalyst was synthesized by in situ electrochemical transformation method with Ru/CoO as the starting material. Briefly, CoO nanorod arrays were first fabricated on carbon fiber paper or fluorine-doped tin oxide (FTO) substrates by cation exchange methodology. Afterwards, ruthenium precursor solution was prepared by dissolving RuCl$_3$ in ethanol/water ($V_{\text{ethanol}}/V_{\text{water}} \approx 1$) to achieve a 30 mM RuCl$_3$ solution. Then, CoO nanorods were immersed in 40 mL of ultrapure water, and an appropriate amount of ruthenium precursor solution was added, aged for 6 h, dried at room temperature, and then heated by $N_2$ flow at 400, 500, and 550 °C for 0.5 h to obtain RuO$_2$ with average particle sizes of 2, 3, and 4 nm, respectively (Supplementary Fig. 38). Note that the Ru loading mass on CoO nanorods can be easily controlled by tuning the adding volumes of ruthenium precursor solution. Finally, the obtained RuO$_2$/CoO nanorods were electrochemically oxidized by scanning cyclic voltammetry between 0.80–1.50 V$_{\text{RHE}}$ to attain RuO$_2$/CoO$_x$ catalysts (Supplementary Fig. 8). The loading mass of RuO$_2$ on CoO$_x$ after optimization is 10 µg on per cm$^2$ electrode (Supplementary Fig. 26 and Supplementary Table 3). For the synthesis of RuO$_2$ reference catalyst, a similar method was applied using carbon black as the support material. The loading mass of RuO$_2$ on carbon black after optimization is 84 µg on per cm$^2$ electrode (Supplementary Fig. 27 and Supplementary Table 4). RuO$_2$ with this loading mass was characterized in Figs. 3 and 4 as reference sample.

**Materials characterization**

Scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images were performed on a Hitachi S-4800 SEM and a JEOL 2100 TEM, respectively. HAADF-STEM images were collected on a JEOL ARM200F microscope with a STEM aberration corrector operated at 200 kV. The convergent semi angle and collection angle were 21.5 and 200 mrad, respectively. EELS spectra were collected using a Titan Themis CUBED G2 60-300 operated at 200 kV. EPR measurements were carried out on a JEOL JES-FA200. The inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed on an Agilent 7700x. X-ray diffraction (XRD) characterization was carried out on a Bruker D8 Advance diffractometer with Cu Kα radiation. The X-ray absorption fine structure spectra of Ru K-edge were performed at 489A beamline in Beijing Synchrotron Radiation Facility (BSRF). The storage rings of BSRF was operated at 2.5 GeV with a stable current of 400 mA. The OER Faradaic efficiency of RuO$_2$/CoO$_x$ was measured by a gas chromatograph (GC-2014, Shimadzu, Japan) equipped with a thermal conductivity cell detector.

In situ spectroscopic characterizations

In situ XPS spectra were measured by ambient pressure XPS end station equipped with a static electrochemical cell at NSRRC TLS BL24A (Supplementary Fig. 12a). The counter electrode was a Pt wire and the reference electrode was a Pt wire coated with Ag/AgCl paste. The working electrode was a carbon paper loaded with RuO$_2$/CoO$_x$ catalysts, which was cut into a circle with a diameter of 5.5 mm. During in situ XPS test, both the counter and reference electrodes were immersed in the electrolyte and sealed by a Nafion membrane and the carbon paper was sandwiched between the Nafion membrane and a Ta foil for electrical contact (Supplementary Fig. 12b). The analysis chamber pressure is around 0.3 mbar due to water diffusing onto the sample's surface and evaporating into the chamber while in situ XPS spectra were measured.

In situ UV–vis spectroscopy was performed on a Hitachi U-3010 with a homemade photo-electrochemical cell, with catalysts fabricated in situ on a FTO substrate as the working electrode, a Pt wire as counter electrode and an Ag/AgCl electrode as the reference electrode.

In situ attenuated reflectance surface-enhanced IR spectra were collected on a Fourier transform infrared spectrometer (Nicolet ISSO, Thermo Fisher Scientific Co., Ltd) with a MCT detector and a Pike Technologies VeeMAX III ATR accessory. A catalyst ink was prepared by mixing 2 mg of catalyst investigated with 1 mL of ultrapure water and then deposited on an Au film coated Si prism. The Si prism, a Pt foil and an Ag/AgCl electrode were served as the working electrode, the counter electrode, and the reference electrode, respectively, in an H-type electrochemical cell, which was separated by a Nafion 115 membrane. All background curves were collected without applied potential in $N_2$-saturated electrolyte, and all spectra were collected with a 4 cm$^{-1}$ resolution.

**EPR tests**

RuO$_2$/CoO$_x$ was treated at 1.00, 1.20, 1.40, 1.60, 1.80 and 2.00 V$_{\text{RHE}}$ for 5 min, respectively, and then dried quickly by high-purity $N_2$. The EPR spectra were collected at a modulation amplitude of 0.8 mT, a modulation frequency of 100 kHz, a conversion time of 50 ms and a time constant of 50 ms. During test, the temperature was set at 70 K. Quantitative analysis was conducted by double integration after baseline correction.

**KIE measurements**

According to previous literature, multicycles chronocoulometric tests were carried out in 1.0 M phosphate buffered saline (PBS) with $H_2^{16}$O and $H_2^{18}$O. The KIE value was estimated from the following: $K_{\text{KIE}} = \frac{I_{\text{H}_2^{16}O}}{I_{\text{H}_2^{18}O}}$.
where \( J_{\text{H}_2^{16}O} \) and \( J_{\text{H}_2^{18}O} \) are the average current density in \( \text{H}_2^{16}O \) and \( \text{H}_2^{18}O \), respectively. The average current density values of multicycles were linear fitted. The KIE value was estimated from the ratio of the two data points in the two fitted line in \( \text{H}_2^{16}O \) and \( \text{H}_2^{18}O \) (Supplementary Fig. 3).

Electrochemical characterizations
The electrochemical performance of the catalysts in neutral (1.0 M PBS) and alkaline (1.0 M KOH) electrolytes was tested in a three-electrode system. A catalyst ink was prepared by ultrasonically dispersing 2 mg of catalyst, 2 mg of conductive carbon (Vulcan XC 72), 20 μL of 5 wt% Naion solution and 20 μL of isopropanol in ultrapure water to achieve a catalyst concentration of 5 mg mL\(^{-1}\). 10 μL of as-prepared catalyst ink was then dropped onto a polished glassy carbon rotating electrode (5 mm in diameter, Pine Research Instrumentation) serving as the working electrode (Supplementary Tables 3 and 4). The counter electrode was a Pt wire and the reference electrode was a calomel electrode saturated in KCl. The electrochemical tests were performed in O\(_2\)-saturated electrolyte with the working electrode rotating at a speed of 1600 rpm. All potentials were referenced to the RHE by using pure hydrogen calibration and corrected with 75% IR loss, and all polarization curves were obtained with a scan rate of 5 mV s\(^{-1}\).

Computational methods
All spin-polarized DFT calculations were performed using Vienna Ab initio Simulation Package (VASP)\(^{43-46}\). The projector augmented wave (PAW) potentials\(^{47}\) and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional\(^{48}\) were adopted in the calculations with a plane wave kinetic energy cut-off of 400 eV. The energy converge criteria was set to 0.05 eV Å\(^{-1}\). All potentials were referenced to the PBS) and alkaline (1.0 M KOH) electrolytes was tested in a three-electrode system. A catalyst ink was prepared by ultrasonically dispersing 2 mg of catalyst, 2 mg of conductive carbon (Vulcan XC 72), 20 μL of 5 wt% Naion solution and 20 μL of isopropanol in ultrapure water to achieve a catalyst concentration of 5 mg mL\(^{-1}\). 10 μL of as-prepared catalyst ink was then dropped onto a polished glassy carbon rotating electrode (5 mm in diameter, Pine Research Instrumentation) serving as the working electrode (Supplementary Tables 3 and 4). The counter electrode was a Pt wire and the reference electrode was a calomel electrode saturated in KCl. The electrochemical tests were performed in O\(_2\)-saturated electrolyte with the working electrode rotating at a speed of 1600 rpm. All potentials were referenced to the RHE by using pure hydrogen calibration and corrected with 75% IR loss, and all polarization curves were obtained with a scan rate of 5 mV s\(^{-1}\).

\[ \Delta G = \Delta E + \Delta ZPE - T \Delta S - eU \]

where \( \Delta G \) is the energy difference of a given reaction, \( \Delta ZPE \) is the zero-point energy correction, \( \Delta S \) is the vibrational entropy change at a given temperature, \( e \) is the elementary charge, and \( U \) is the electrode potential.

Data availability
The data that support the findings of this study are available from the corresponding author on reasonable request.

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Author contributions
T.L. conceived the project, designed the experiments, and wrote the manuscript. K.D. and J.X.G. performed the experiments. L.F.Z. constructed models and conducted the DFT calculations guided by Z.H., and Z.H. designed some experiments to verify the correlation between theoretical models and experimental observations. C.Y. and C.W. performed the in situ XPS measurements. J.Q.S. commented and revised the manuscript. J.M. carried out the TEM and HADDF-STEM characterizations. All authors discussed the results and commented on the manuscript.

Competing interests
The authors declare no competing interests.

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