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Regulating Co–O covalency to manipulate mechanistic transformation for enhancing activity/durability in acidic water oxidation†

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Developing earth-abundant electrocatalysts with high activity and durability for acidic oxygen evolution reaction is essential for H₂ production, yet it remains greatly challenging. Here, guided by theoretical calculations, the challenge of overcoming the balance between catalytic activity and dynamic durability for acidic OER in Co₃O₄ was effectively addressed *via* the preferential substitution of Ru for the Co²⁺ (T_d) site of Co₃O₄. *In situ* characterization and DFT calculations show that the enhanced Co–O covalency after the introduction of Ru SAs facilitates the generation of OH* species and mitigates the unstable structure transformation *via* direct O–O coupling. The designed Ru SAs-CoO_x catalyst (5.16 wt% Ru) exhibits enhanced OER activity (188 mV overpotential at 10 mA cm⁻²) and durability, outperforming most reported Co₃O₄-based and Ru-based electrocatalysts in acidic media.

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Introduction

Electrocatalytic water splitting is considered a promising approach for producing clean and renewable hydrogen owing to its high energy conversion efficiency and safety.^{1–7} To date, acidic water electrolyzers exhibit great advantages compared with conventional alkaline water electrolyzers, such as lower ohmic losses, higher voltage efficiency and faster system response.^{8–10} More importantly, the smaller gas crossover in acidic electrolyzers avoids the mixture of H₂ and O₂, which ensures higher gas purity (note S1†).^{11,12} The acidic oxygen evolution reaction (OER) as the key half-reaction contributes to a major energy loss in overall electrochemical water splitting, which limits the efficiency of the overall process. Compared to

the alkaline OER, acidic OER exhibits inferior catalytic activity due to the following two reasons: (1) the oxidation of adsorbed hydroxyl (OH*) into O₂ remains challenging in acidic media due to the scarcity of hydroxide anions (OH⁻), resulting in lower OH* coverage on the catalyst surface. (2) The inferior durability of earth-abundant electrocatalysts (*e.g.*, Fe, Co, and Ni-based) in acidic electrolytes compared to that in alkaline electrolytes hinders their practical application.

To achieve efficient acidic water splitting, various catalysts with noble metal iridium (Ir) or ruthenium (Ru) as active sites have been widely studied, such as pyrochlore-type material Y₂Ru₂O_{7-δ},¹³ bimetal oxide material (Li_xRuO₂ and¹⁴ Cr_{0.6}Ru_{0.4}O₂,¹⁵) and perovskite-like material (SrTi_{1-x}Ir_xO₃ and¹⁶ Sr₂MIr(v)O₆,¹⁷). However, the high cost and scarcity of noble metals limit their large-scale applications. Cobalt oxide (Co₃O₄) as an earth-abundant material has been theoretically predicted as a potential catalyst for the OER due to (1) the optimum binding energy with the O-intermediates, which is comparable to that of RuO₂;¹⁸ (2) remarkable static durability (resting state or open-circuit potential) in acidic media owing to the relatively strong overlapping of the octahedral Co³⁺(O_h)–O orbital.¹⁹ However, its practical catalytic performance in acidic media is not satisfactory: (1) compared that in alkaline media with abundant OH⁻, the OH* coverage on the catalyst surface in acidic media is comparatively lower; (2) in the conventional adsorbate evolution mechanism (AEM) process, the multiple processes preceding the formation of the O–O bond result in frequent valence changes, which facilitate surface reconstruction and limit the durability (Fig. S1a,† step 1–3).^{20–22} Thereby, to enhance the activity and durability of Co₃O₄ for acidic OER, the local bonding environment is considered to be regulated to

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optimize the reaction process. With these considerations, a second adsorption site (lattice oxygen) is utilized to promote the direct O–O coupling during the OER process, namely the lattice oxygen oxidation mechanism (LOM). Direct O–O coupling not only mitigates the unstable reconstruction process before the formation of the O–O bond (Fig. S1b†), but also has the potential to surpass the theoretical limitation of activity in the conventional AEM.^{23–26}

In order to facilitate the reaction pathway for direct O–O coupling, the moderate orbital overlap of metal–oxygen (M–O covalency) is essential.^{24,27,28} Specifically, the enhanced M–O covalency results in a decreased energy gap between the metal d and O 2p band center, thereby moving the Fermi level closer to the O 2p-band center and the redox potential of the O₂/H₂O couple, which is thermodynamically favorable for the redox of lattice oxygen.^{29,30} Nevertheless, excessive covalency would cause an improved lattice oxygen migration rate compared to the vacancy filling rate during the LOM cycles, leading to structure destabilization.^{5,31} Therefore, we propose that moderate Co–O covalency of Co₃O₄ is more advantageous for enhancing durability compared to the AEM process by mitigating the unstable reconstruction process. In the present study, guided by the theoretical calculations, we design an electrocatalyst composed of Ru single atom (5.16 wt%) doped cobalt oxide (Ru SAs-CoO_x) to overcome the activity/durability tradeoff for acidic OER. Our theoretical calculations suggest that (1) the introduction of heteroatom Ru could benefit the generation of OH* species, thus providing plentiful OH* species for the subsequent oxidation process;²⁵ (2) the introduction of Ru allows the enhanced orbital overlap between the Co 3d and O 2p, thus increasing the Co–O covalency;²⁸ (3) the doping of Ru promotes the generation of oxygen vacancies (O_v), facilitating direct O–O coupling during the OER process and the oxygen evolution from lattice oxygen.^{19,32,33} *In situ* ¹⁸O isotope labeling differential electrochemical mass spectrometry (DEMS) demonstrated Ru to be the switch promoting oxygen evolution from lattice oxygen. In addition, *in situ* Raman spectroscopy suggested that the growth of stable amorphous cobalt oxide on the electrode surface acted as the protective layer enhancing the durability. As a result, the prepared Ru SAs-CoO_x catalyst delivers a low overpotential of 188 mV at a current density of 10 mA cm⁻², and enhanced long-term durability in acidic media, which are superior to those of pristine Co₃O₄ (395 mV at 10 mA cm⁻²) and commercial RuO₂ (312 mV at 10 mA cm⁻²).

Results and discussion

Theoretical prediction for the structure of the electrocatalyst

Density functional theory (DFT) calculations were first performed to investigate the participation of the lattice oxygen oxidation reaction of Ru SAs-CoO_x. To ascertain the doping position of Ru, we compared the formation energy for the substitution of tetrahedral Co²⁺ (T_d) and octahedral Co³⁺ (O_h) sites for a single Ru atom, which could effectively explore the influence of the doping element on the local reaction environment. As displayed in Fig. S2–S3,† replacing Co²⁺ (T_d) with Ru leads to a lower barrier (1.194 eV) compared to that of the Co³⁺

(O_h) site (2.803 eV), indicating a thermodynamically preferred replacement of Ru atoms at the Co²⁺ (T_d) site. Then, to evaluate the feasibility of the lattice oxygen oxidation reaction after Ru doping, the Co–O covalency and O_v formation energy of Co₃O₄ and Ru–Co₃O₄ are calculated, respectively. As illustrated in Fig. 1a–c and Table S1,† the substitution of divalent tetrahedral Co²⁺ (T_d) with Ru³⁺ reduces the localized gap between the Co 3d and O 2p band center, accompanied by an increased orbital overlap between Co 3d and O 2p. Therefore, the antibonding states below the Fermi level displayed a higher oxygen character that results in the enhanced Co–O covalency, which would thermodynamically promote the oxidation of lattice oxygen.^{34,35}

Besides, considering the crucial role of O_v formation in facilitating direct O–O coupling, the O_v formation energy in Co₃O₄ and Ru–Co₃O₄ is also calculated. The formation energies of four different types of O_v in Co₃O₄ are 1.509, 0.450, 2.863, and 2.820 eV, respectively (Fig. S4†). In the case of Ru–Co₃O₄, the corresponding formation energies for these four types of O_v are 0.149, 0.362, 1.676, and 1.362 eV (Fig. S5†). It is clear that the substitution of Co with Ru significantly reduces the formation energy of O_v. Therefore, the increased Co–O covalency and the lower O_v formation energy facilitate the transformation of the OER mechanism from a conventional adsorbate evolution mechanism (AEM, OH attack) to a lattice oxygen oxidation mechanism (LOM, O–O coupling) (Fig. 1d).^{32,33} In addition, it is worth noting that it is difficult to carry out accurate DFT studies to represent the exact surface of the electrocatalyst and the local experimental conditions. However, DFT calculations here may provide side insight for the design of electrocatalysts and lateral understanding of the structural and catalytic mechanism changes after the incorporation of Ru.

Material synthesis and characterization

Guided by the theoretical prediction results, we synthesized Ru SAs-CoO_x by a cation exchange method. The detailed synthetic procedure and structural changes are illustrated in Fig. S6† and 2a. First, a cobalt precursor (Co-pre) with “flower-like” morphology (Fig. S7 and S8a–b†) was prepared *via* co-precipitation of Co(CH₃COO)₂·4H₂O and polyvinylpyrrolidone (PVP) in ethylene glycol under the protection of argon at 170 °C. Herein, PVP was employed to improve the uniformity of the final architecture. Next, the prepared Co-pre was annealed at 300 °C to yield the pristine Co₃O₄ nanoflower (Fig. S8c–d†). Subsequently, the Co₃O₄ nanoflower (10 mg) was added into the ruthenium chloride (0.075 mmol) solution and stirred at 60 °C for the cation exchange reaction (5.16 wt% Ru). Finally, the Ru SAs-CoO_x sample was obtained after calcination at 300 °C, which could detach the chloride ligands and improve crystallization.^{36,37}

X-ray diffraction (XRD) was employed to investigate the crystal structure of Co₃O₄ and Ru SAs-CoO_x. As depicted in Fig. 2b–c, the diffraction peaks of Co₃O₄ were exhibited in the XRD pattern of Ru SAs-CoO_x, and no diffraction peaks corresponding to Ru-related species could be detected, suggesting that the Ru species were highly dispersed or amorphous.³⁸ However, the incorporation of Ru³⁺ with a larger ionic radius



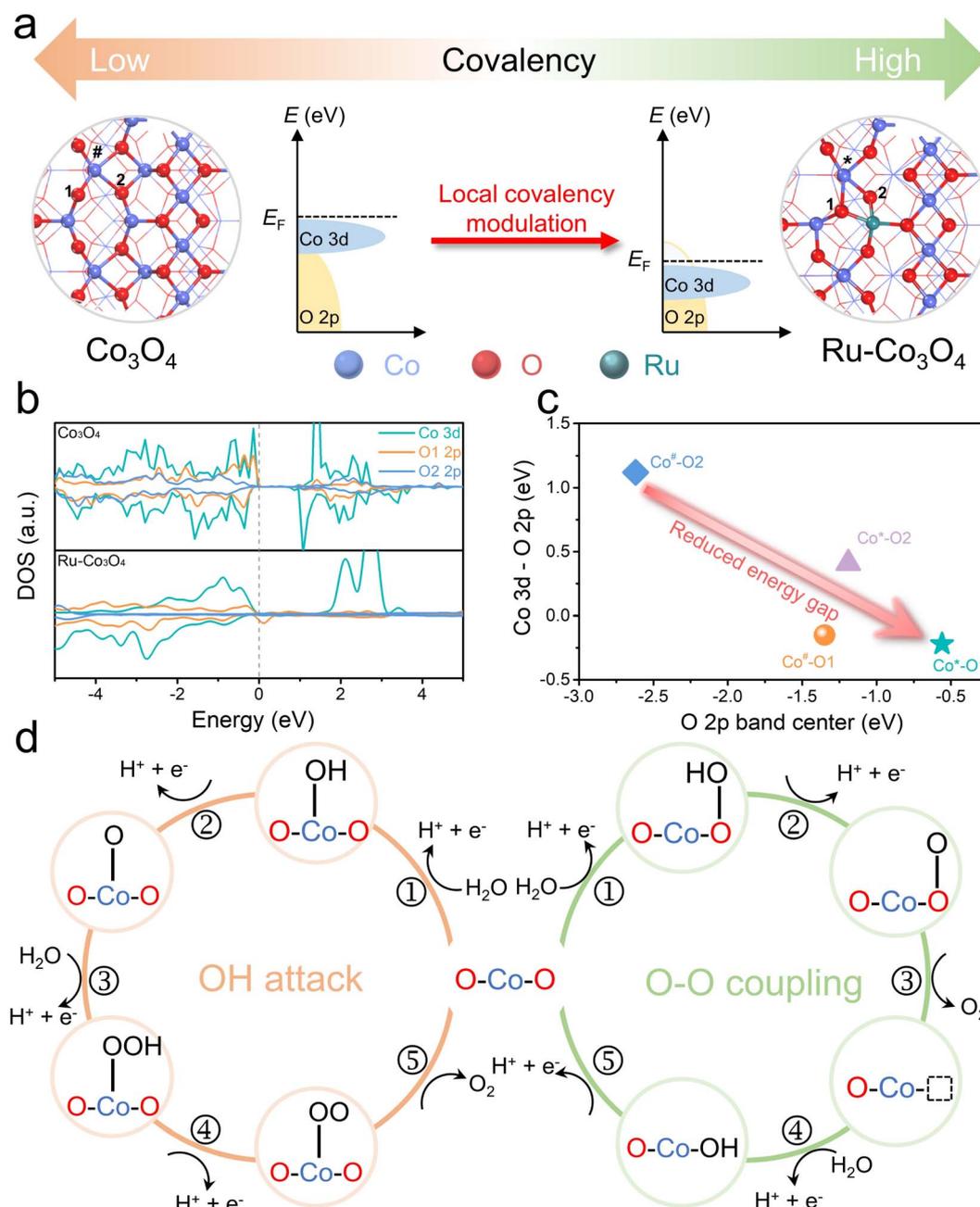


Fig. 1 Electronic structures and OER pathways. (a) Structures and schematic energy bands of Co_3O_4 and $\text{Ru-Co}_3\text{O}_4$ (the corresponding structure is shown in Fig. S5a†). (b) Computed DOS of Co 3d and O 2p for Co_3O_4 and $\text{Ru-Co}_3\text{O}_4$. (c) Energy gap between Co 3d and O 2p versus the O 2p band center for Co_3O_4 and $\text{Ru-Co}_3\text{O}_4$. (d) Proposed transformation of the OER mechanism from the AEM to LOM after the doping of Ru.

resulted in an increase in micro-strain within the Co_3O_4 lattice. Consequently, Ru SAs- CoO_x displayed a clear XRD peak width broadening ($\sim 0.3^\circ$), as well as a negative diffraction peak shift ($\sim 0.2^\circ$) compared to pristine Co_3O_4 , which confirmed that the incorporation of Ru is not limited to the surface but extends into the Co_3O_4 framework.^{38,39} Besides, the broad peak observed between 20° and 30° can be attributed to the presence of carbon residue primarily derived from ethylene glycol and $\text{Co}(\text{CH}_3\text{-COO})_2$. The morphologies of Ru SAs- CoO_x were then examined

using transmission electron microscopy (TEM). As shown in Fig. 2d and S9–S10,† after introducing Ru atoms, Co_3O_4 was transformed into the disordered nanosheet structure, where the interconnected nanostructures with certain amounts of holes could be observed. The N_2 adsorption–desorption isotherms and the corresponding Brunauer–Emmett–Teller (BET) analysis showed that the surface area of Ru SAs- CoO_x ($155.46 \text{ m}^2 \text{ g}^{-1}$) was higher than that of pristine Co_3O_4 ($33.73 \text{ m}^2 \text{ g}^{-1}$), while the average pore size of Ru SAs- CoO_x (4.41 nm) was found to be



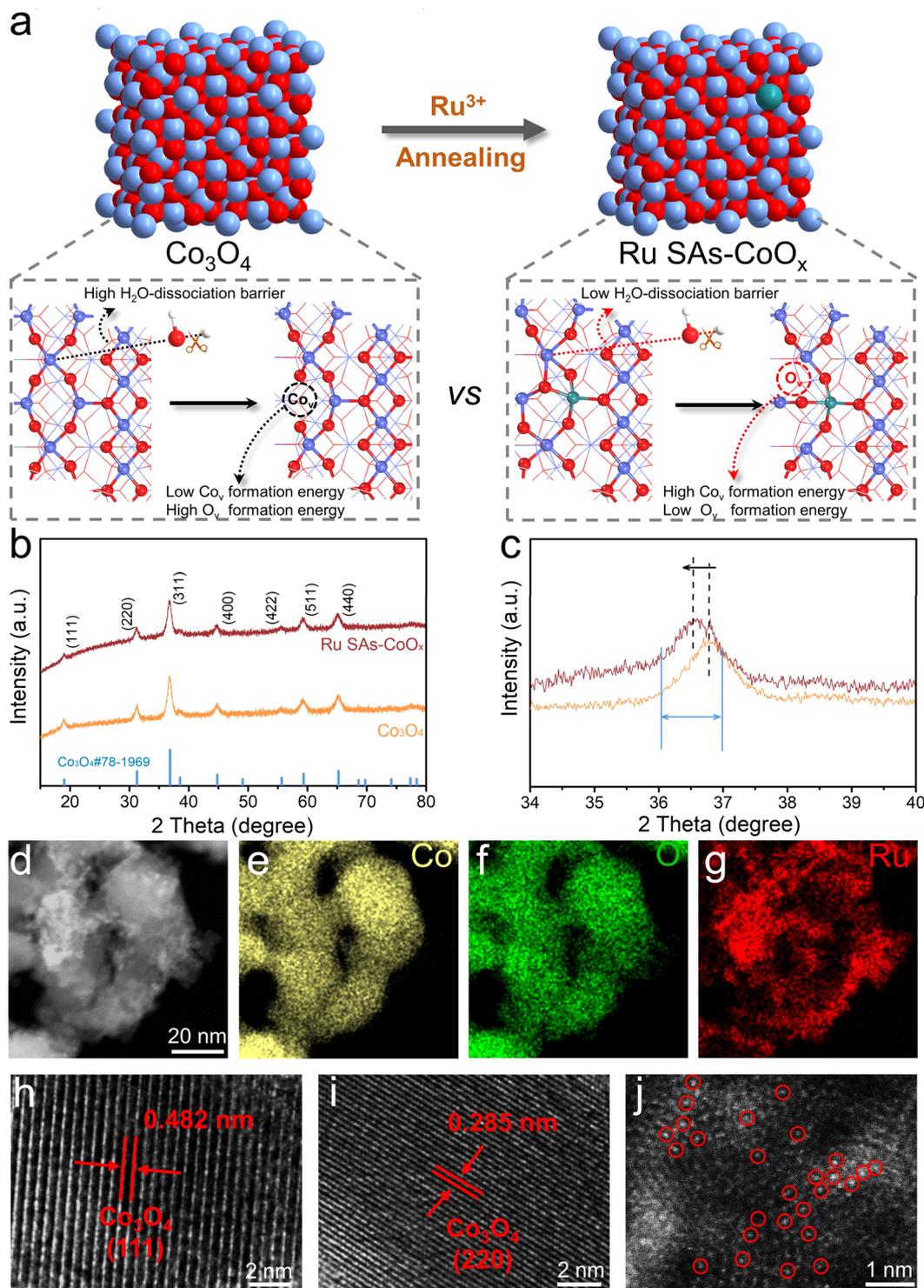


Fig. 2 Schematic illustration of the synthesis, mechanism, and morphological characterization studies. (a) The synthetic procedure and mechanism of Ru SAs-CoO_x as an efficient electrocatalyst for acidic OER. (b) XRD patterns of Ru SAs-CoO_x and Co₃O₄ (ca. 3° min⁻¹). (c) Enlarged XRD pattern of Ru SAs-CoO_x and Co₃O₄. (d–g) HAADF-STEM images of Ru SAs-CoO_x and the corresponding elemental mapping images of Co, O, and Ru. (h and i) HRTEM images of Ru SAs-CoO_x. (j) Atomic-resolution HAADF-STEM image of Ru SAs-CoO_x. Ru atoms (marked by red circles) are uniformly distributed on the surface of CoO_x.

smaller compared with that of pristine Co₃O₄ (13.27 nm) (Fig. S11†). The above-mentioned results were attributed to the “etching-recombination” that occurred during the cation

exchange process, which led to an increased surface area, and exposed more sites for the electrocatalysis of the OER. In addition, the elemental mapping images indicated the uniform



distribution of Ru, Co, and O atoms in the selected porous nanosheets, confirming the successful introduction of Ru after the cation exchange process (Fig. 2e–g). More structural features of Ru SAs-CoO_x were then explored by high-resolution transmission electron microscopy (HRTEM). Two obvious continuous and ordered lattice fringes with lattice spacings of 0.482 and 0.285 nm were observed, which corresponded to the (111) and (220) planes of Co₃O₄ (Fig. 2h–i). No lattice fringes derived from Ru nanoparticles could be found. From the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, numerous atomically dispersed bright dots (highlighted with red circles) of Ru atoms were homogeneously distributed on the surface of Ru SAs-CoO_x, confirming that Ru species were anchored on Co₃O₄ in the form of single-atoms during the cation exchange process (Fig. 2j and S12†).^{40–42}

Electron spin resonance (ESR) measurements were performed to investigate the generation of O_v, and the signal corresponding to the electron trapped on O_v was detected at $g = 2.003$. As shown in Fig. 3a, a stronger signal intensity of Ru SAs-CoO_x was exhibited relative to pristine Co₃O₄, demonstrating

higher O_v concentration.⁴³ To further substantiate the association between the increase in O_v concentration and Ru doping, Ru-CoO_x catalysts with different Ru contents were prepared by varying the dosage of Ru³⁺ (*i.e.*, 0.025 mmol, 0.05 mmol, and 0.075 mmol). The resulting products were denoted as Ru-CoO_x-0.025, Ru-CoO_x-0.05, and Ru-CoO_x-0.075 (*i.e.* Ru SAs-CoO_x), respectively. The results of ESR also showed that the O_v concentration increased significantly with the enhancement of Ru content (from 0 to 5.16 wt% measured by ICP-AES) (Fig. S13†).

XPS spectra were also measured to elucidate the chemical compositions and valence state of the prepared electrocatalysts (Fig. S14–S15†). For the Co 2p spectrum of Ru SAs-CoO_x, two major peaks located at 779.3 and 794.7 eV were assigned to Co 2p_{3/2} and Co 2p_{1/2}, which were fitted by two regions of Co²⁺ and Co³⁺. The relative atomic ratio of Co²⁺/Co³⁺ could be obtained by comparing the area of the fitted curve. As more oxygen vacancies were generated on the surface of Ru SAs-CoO_x, the ratio of Co²⁺/Co³⁺ in Ru SAs-CoO_x was expected to increase.^{44,45} However, the ratio of Co²⁺/Co³⁺ for the O_v-rich Ru SAs-CoO_x

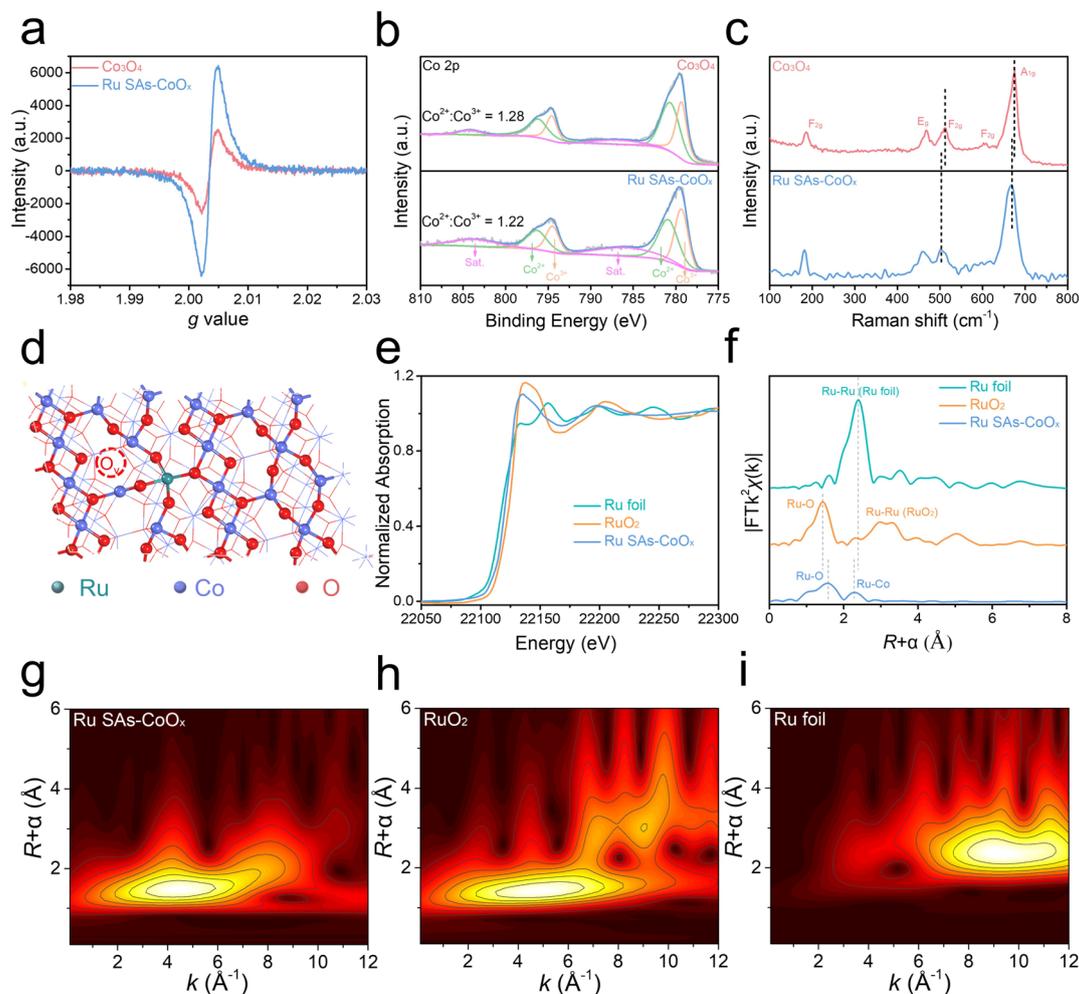


Fig. 3 Structure characterization of Ru SAs-CoO_x. (a) ESR spectra of Ru SAs-CoO_x and Co₃O₄. (b) Co 2p XPS spectra of Ru SAs-CoO_x and Co₃O₄. (c) Raman spectra of Ru SAs-CoO_x and Co₃O₄. (d) Structure of Ru SAs-CoO_x. (e) Ru K-edge XANES spectra of Ru SAs-CoO_x, Ru foil, and RuO₂. (f) Fourier-transformed Ru K-edge EXAFS spectrum of Ru SAs-CoO_x, Ru foil, and RuO₂. (g–i) Wavelet transforms for the k^2 -weighted Ru K-edge EXAFS signals of Ru SAs-CoO_x, Ru foil, and RuO₂.



(1.22) showed a slight decrease compared to that of the pristine Co_3O_4 (1.28) (Fig. 3b), which indicated that the Ru atoms were doped into the Co_3O_4 framework to maintain electrical neutrality, rather than being adsorbed on the surface. In addition, the ratio of $\text{Co}^{2+}/\text{Co}^{3+}$ for Ru SAS- CoO_x (1.22) showed a slight decrease compared to that of the pristine Co_3O_4 (1.28), which suggested that Ru preferentially occupied T_d sites ($\sim 78\%$, note S2†).^{46,47} In the Ru 3p spectrum (Fig. S14d†), the peaks of Ru 3p_{3/2} and Ru 3p_{1/2} located at 462.60 and 484.88 eV were detected, which are positioned between those of Ru (0) and Ru (iv),⁴⁸ demonstrating that the oxidation state of Ru in Ru SAS- CoO_x was between 0 and +4 (Fig. S16†). Then Raman spectroscopy was conducted to reveal the structural changes in the coordination environment of Co_3O_4 .⁴⁹ As shown in Fig. 3c, five characteristic peaks corresponding to the E_g , F_{2g} , and A_{1g} of Co_3O_4 were detected. Specifically, A_{1g} represented the octahedral (O_h) sites while F_{2g} corresponded to the tetrahedral (T_d) sites. After doping of Ru species, notable shifts in the characteristic peaks of F_{2g} ($\sim 11\text{ cm}^{-1}$) and A_{1g} ($\sim 7\text{ cm}^{-1}$) were observed, providing clear evidence of Ru substitution at both tetrahedral (T_d) and octahedral (O_h) sites. The larger shift for F_{2g} than that for A_{1g} suggests that the Ru preferentially occupied the T_d sites (Fig. 3d).⁴⁹ In order to investigate the local coordination of Ru species in Ru SAS- CoO_x , the Ru *K*-edge region X-ray absorption near edge structure (XANES) was measured, which displayed clear differences from those of Ru foil and RuO_2 (Fig. 3e). Extended X-ray absorption fine structure (EXAFS) for Ru SAS- CoO_x was performed to analyze the bonding forms of Ru species. The peak at 1.57 Å was associated with the back scatterings between Ru and neighboring O in Ru SAS- CoO_x . Another peak at 2.29 Å could be attributed to the back scatterings between metal and metal. Furthermore, quantitative EXAFS curve-fitting analyses for Ru SAS- CoO_x revealed that the average coordination number between Ru and O was 3.7 (Fig. S17 and Table S2†), which further demonstrates the preference of Ru substitution at the T_d site (a 4-coordination structure) over the O_h site (6-coordination structure). Additionally, the presence of O_v may contribute to a further decrease in the average coordination number. The wavelet transform (WT) analysis of the EXAFS spectrum was performed to further confirm the formation of Ru SAS (Fig. 3g–i). Only one intensity maximum at about 4.5 Å^{-1} (Ru–O scattering path) was detected in the WT contour plot of Ru SAS- CoO_x . The signal corresponding to $\text{Ru}_B\text{–O–Co}_B$ was not detected, which may be due to its weaker coordination.

Electrocatalytic performance of the OER in acidic media

The electrocatalytic performances of the prepared catalysts were evaluated with a three-electrode system at room temperature. The *iR*-corrected polarization curves recorded by linear scan voltammetry (LSV) in N_2 -saturated 0.1 M HClO_4 electrolyte were displayed. When the content of Ru reached 5.16 wt% (Fig. S18–S24 and Tables S3 and S4†) in the obtained Ru- CoO_x (Ru SAS- CoO_x) catalyst, it showed a minimum overpotential of 188 mV at a current density of 10 mA cm^{-2} , which was much smaller than that of commercial RuO_2 (312 mV) and pristine Co_3O_4 (395 mV) (Fig. 4a). Then the Tafel slopes derived from the polarization

curves were used to evaluate the catalytic kinetics. As shown in Fig. 4b, the Tafel slope of Ru SAS- CoO_x was calculated to be 63 mV dec^{-1} , which was much lower than that of pristine Co_3O_4 (111 mV dec^{-1}) and commercial RuO_2 (84 mV dec^{-1}), indicating the faster kinetics toward the OER.^{50,51} The Tafel slopes of all samples fell within the range of $60\text{–}120\text{ mV dec}^{-1}$, indicating a mixed kinetic control mechanism where the overall rate is not controlled by a single path.^{20,52–54} Besides, several other points may also cause the value of the Tafel slope to deviate from 60 mV dec^{-1} or 120 mV dec^{-1} : (1) transfer coefficient (α) largely deviates from the commonly assumed value; (2) the coverage would vary as the electrode potential increases, leading to a corresponding alteration in the Tafel slope;[†] (3) the catalytic activity may originate from multiple active sites, limiting the application of the conventional Butler–Volmer formalism. The low overpotential and Tafel slope of Ru SAS- CoO_x also demonstrated its superior performance among Co_3O_4 -based electrocatalysts, which is even well comparable with the reported Ir-based and Ru-based OER electrocatalysts in acidic media, such as Co–RuIr (235 mV at 10 mA cm^{-2}),⁵⁵ Ru@ IrO_x (282 mV at 10 mA cm^{-2}),⁵⁶ amorphous IrO_2 (255 mV at 10 mA cm^{-2}),⁵⁷ $\text{Ba}_2\text{–YrO}_6$ (318 mV at 10 mA cm^{-2}),⁵⁸ Ir–STO (295 mV at 10 mA cm^{-2}),⁵⁹ and $\text{RuNi}_2\text{@G-250}$ (210 mV at 10 mA cm^{-2})⁶⁰ (Fig. 4c and Table S5†). In addition, the exchange current density (j_0) of Ru SAS- CoO_x (0.033 mA cm^{-2}) could be evaluated by extrapolating the Tafel slope (Fig. S25†), which was much higher than those of pristine Co_3O_4 (0.004 mA cm^{-2}) and commercial RuO_2 (0.012 mA cm^{-2}), demonstrating the fast electron transfer rate between the electrode and Ru SAS- CoO_x catalyst surface.

We further investigated the electrochemical surface area (ECSA) of Ru SAS- CoO_x by testing the double layer capacitances (C_{dl}). Compared with those of pristine Co_3O_4 (0.5 mF cm^{-2}) and RuO_2 (14.5 mF cm^{-2}), the larger C_{dl} value (18.6 mF cm^{-2}) suggested that more electrochemical surface area was generated (Fig. S26†). Considering that the changes in morphology would impact the activity, different elements (Mn, Fe, and Ni) were introduced to explore their morphologies and catalytic activity. As shown in Fig. S27–S29,† after the introduction of other different elements, the morphologies all transformed into the nanosheet structure. However, there was no observed enhancement in the catalytic activity. This could be attributed to the fact that compared to these 3d transition metals, Ru exhibited stronger capacity for H_2O dissociation, which benefited the generation of OH^* species, thereby facilitating the generation of abundant OH^* species and subsequently enhancing catalytic activity. Therefore, the introduction of Ru was primarily responsible for the observed enhancement in catalytic activity. Turnover frequencies (TOFs) as another important parameter could be applied to evaluate the intrinsic activity per site of the catalyst.^{13,44,61} Although many methods have been applied to estimate the number of active sites, accurate estimation of the TOF is still a challenge. Here, the lower limit TOF of the Ru SAS- CoO_x and RuO_2 electrodes was estimated by making an approximation that all metal centers in the catalysts are available for the OER.^{62–64} As displayed in Fig. 4d, the lower limit TOF value of Ru SAS- CoO_x at 1.5 V is as high as 0.02 s^{-1} , 7.7 times higher than that of RuO_2 . The



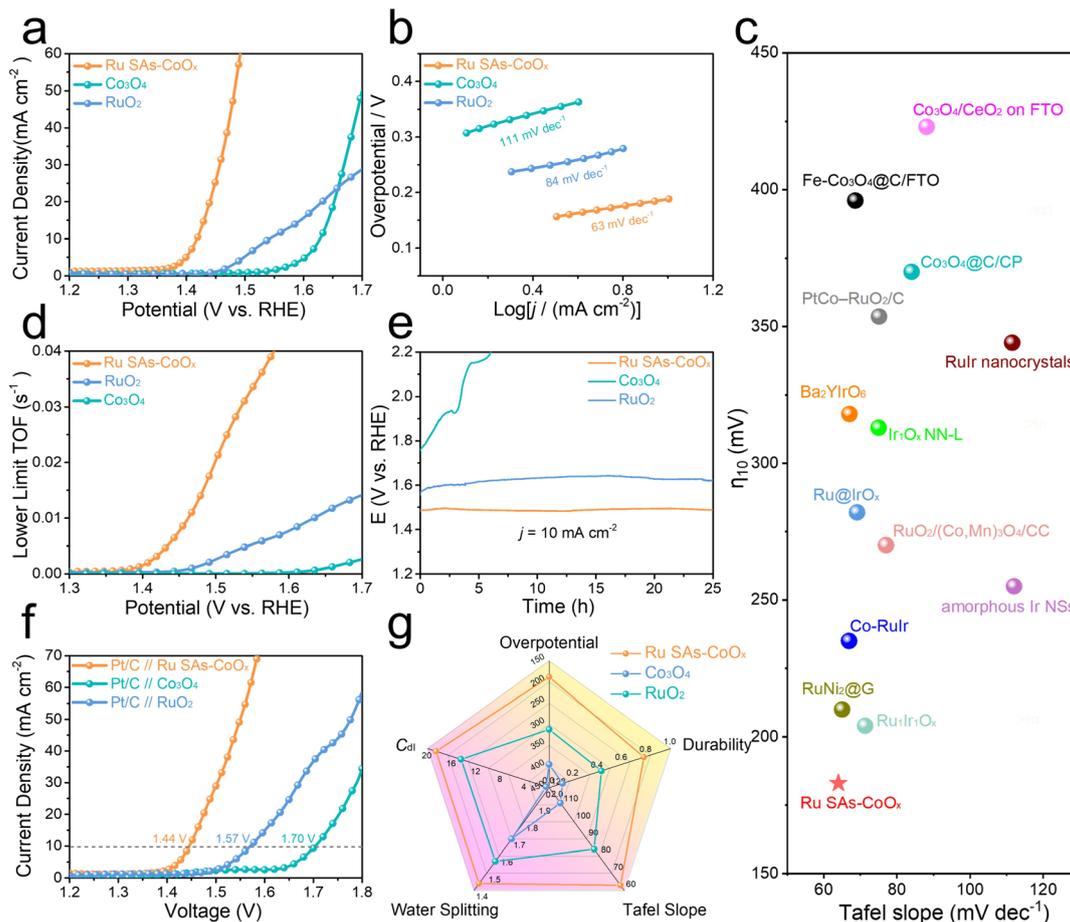


Fig. 4 Catalytic activity for the OER and overall water splitting. (a and b) OER polarization curves and corresponding Tafel slopes of Ru SAs-CoO_x, Co₃O₄, and RuO₂. (c) Comparison with the recently reported Ru-based, Ir-based, and Co-based OER electrocatalysts. (d) Lower limit TOF curves of Ru SAs-CoO_x, Co₃O₄, and RuO₂. (e) Chronopotentiometric curves of Ru SAs-CoO_x, Co₃O₄, and RuO₂ recorded at a constant current density of 10 mA cm⁻². (f) Polarization curves of the Pt/C//Ru SAs-CoO_x, Pt/C//Co₃O₄, and Pt/C//RuO₂ electrolyzers for overall water splitting. (g) Comparison of overpotential (mV @ 10 mA cm⁻²), durability (current retention ratio), Tafel slope (mV dec⁻¹), water splitting (mV @ 10 mA cm⁻²), and C_{dl} (mF cm⁻²) for Ru SAs-CoO_x, Co₃O₄, and RuO₂.

faradaic efficiency of nearly 100% for the OER on Ru SAs-CoO_x was evaluated by the water drainage method, indicating excellent selectivity for oxygen generation (Fig. S30[†]).

Durability is an important parameter to evaluate the OER performance in acidic media. Chronopotentiometry tests were conducted at a current density of 10 mA cm⁻². As revealed in Fig. 4e, Ru SAs-CoO_x displayed a slight potential change from 1.485 to 1.494 V after 25 hours, which was far better than that of RuO₂ (1.556 V to 1.623 V, aligned with the trend of commercial RuO₂ in the reported literature studies.^{6,9}) and pristine Co₃O₄. Meanwhile, the chronoamperometric curves of Ru SAs-CoO_x, RuO₂ and pristine Co₃O₄ were also recorded at the same initial current density (10 mA cm⁻²). The results indicated that the current retention of Ru SAs-CoO_x after 20 hours was 77.3%, which was superior to RuO₂ (43.3%) and pristine Co₃O₄ (10.6%) (Fig. S31[†]). Meanwhile, the durability of Ru SAs-CoO_x was also compared with previously reported Co₃O₄ electrocatalysts, which also exhibited a significantly better durability (Table S6[†]). After the durability test, the morphology, electronic structure, and composition of the catalysts were studied. As displayed in

Fig. S32–S34,[†] HRTEM and EDS results confirmed that the Ru SAs-CoO_x still maintained a porous structure and all the elements (Ru, Co and O) could be detected. Meanwhile, a slight positive shift was observed in Co 2p and O 1s spectra, confirming an increase in valence state at oxidative potentials. This shift can be attributed to the oxidative conditions during the OER process.^{65,66} The XRD pattern revealed that the Co₃O₄ phase of Ru SAs-CoO_x was well-maintained, although the peak intensity decreased obviously. This decrease was likely due to the surface composition of Ru SAs-CoO_x partially transforming into amorphous species. In addition, inductively coupled plasma mass spectrometry (ICP-MS) was used to monitor the catalyst dissolution rate during chronopotentiometry tests at 10 mA cm⁻² in 0.1 M HClO₄ solution. The results, as indicated in Table S7,[†] revealed very low rates of Ru and Co dissociation.

Owing to its excellent OER activity, an acidic electrolyzer was assembled using Ru SAs-CoO_x as the anode and commercial Pt/C as the cathode. As shown in Fig. 4f, the Pt/C//Ru SAs-CoO_x couple required only 1.44 V to achieve a current density of 10 mA cm⁻², lower than that of the Pt/C//RuO₂ couple (1.57 V at 10



mA cm⁻²) and Pt/C//Co₃O₄ couple (1.70 V at 10 mA cm⁻²). To sum up, compared with pristine Co₃O₄ and RuO₂, Ru SAs-CoO_x exhibited overwhelming advantages for the OER from the aspects of overpotential, Tafel slope, durability, water splitting, and C_{dl} (Fig. 4g).

Understanding the reaction mechanism

To rationalize the enhanced OER activity and durability of Ru SAs-CoO_x, the reaction mechanism was explored. *In situ* ¹⁸O isotope labeling DEMS was used to validate the participation of the LOM during the OER process (Fig. 5a and b). The signals for the mass-to-charge ratio (*m/z*) = 34 were detected in gas production, which included the ¹⁸O in the lattice and ¹⁶O in the water,⁶⁷ confirming the successful ¹⁸O labeling and the

involvement of the LOM during the OER process (Fig. S35†).^{34,68} In contrast, the signals of ³⁴O₂ for pristine Co₃O₄ were not detected, demonstrating that the low Co–O covalency and less O_v concentration of Co₃O₄ would inhibit the LOM process. Therefore, the DEMS measurement confirmed the doping of Ru to be the switch for the transformation of the OER mechanism from the conventional AEM to the LOM.

To unveil the local environment and understand the reaction mechanisms of Ru SAs-CoO_x during the OER process, *in situ* Raman spectroscopy was performed as well. Fig. 5c exhibits the Raman spectra of Ru SAs-CoO_x recorded from 0 to 60 min at 1.5 V. Three characteristic peaks corresponding to the E_g (~465 cm⁻¹), F_{2g} (~505 cm⁻¹), and A_{1g} (~660 cm⁻¹) of Co₃O₄ spinel oxides were detected. With the increase in the OER time, a new

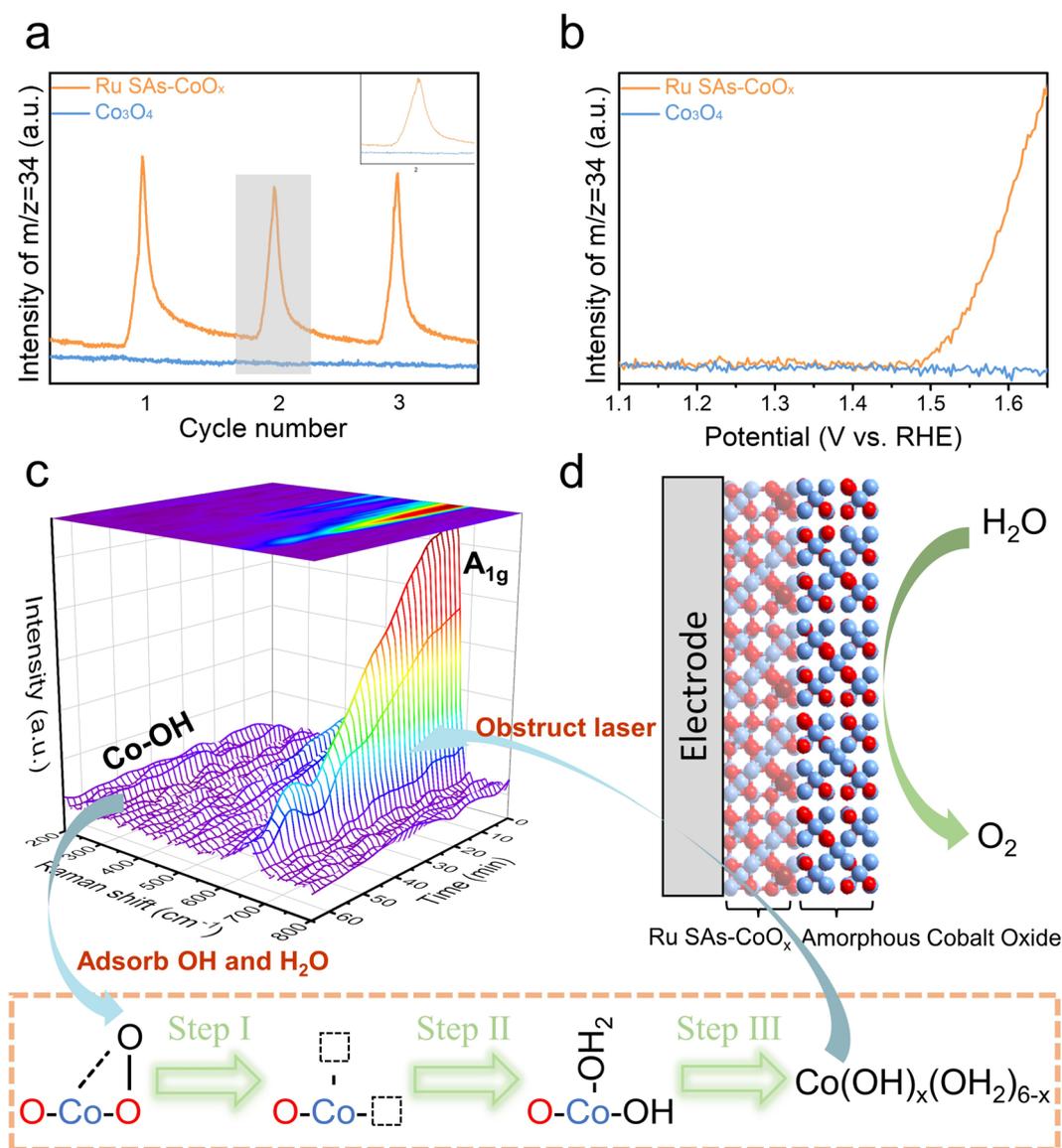


Fig. 5 Mechanism investigation of Ru SAs-CoO_x during the OER process. (a) *In situ* DEMS signals of ³⁴O₂ for ¹⁸O-labeled Ru SAs-CoO_x and Co₃O₄ in 0.1 M HClO₄ relative to time. (b) *In situ* DEMS signals of ³⁴O₂ for ¹⁸O-labeled Ru SAs-CoO_x and Co₃O₄ in 0.1 M HClO₄ relative to potential. (c) *In situ* Raman spectra recorded from 0 to 60 min. (d) Schematic diagram showing the electrochemical environment of Ru SAs-CoO_x during the OER process.



signal corresponding to the chemical bonds between adsorbed OH and Co atoms in the octahedral Co–OH gradually emerged at $\sim 250\text{ cm}^{-1}$ (Fig. S36[†]),^{69,70} suggesting the formation of amorphous Co–OH due to the existence of interim oxygen vacancies during consecutive vacancy filling/lattice oxygen migration in the LOM cycles. Thus, these vacancies could be easily occupied by OH and H₂O to form Co(OH)_x(H₂O)_{6–x}, which would slowly degrade into amorphous cobalt oxide. As a result, the intensity of all the peaks decreased substantially, and the full width at half maximum (FWHM) peak shape was also broadened because the growth of amorphous cobalt oxide obstructed the focal point of the laser.^{19,71} Based on the above results, although the durability was maintained well during the OER process, the surface structure of Ru SAs–CoO_x during the OER process has gradually transformed into an amorphous cobalt oxide layer (Fig. 5d).

DFT calculations were also carried out to shed light on the enhanced catalytic performance of Ru SAs–CoO_x. The related models are constructed based on the experimental analysis. Then the Gibbs free energy of the elementary steps during the OER process is calculated, respectively. First, the traditional AEM pathway is considered for pristine Co₃O₄ and Ru SAs–CoO_x. Since vacancy filling/lattice oxygen migration is not involved in the AEM pathway, the oxygen vacancies are pre-created in the established model (Fig. S37–S39[†]). As shown in Fig. S40,† for the DFT results of the AEM pathway, the Co and Ru sites display a much higher energy barrier than that of the Co site on pristine Co₃O₄. This finding contradicts the observed enhanced catalytic activity of Ru SAs–CoO_x compared to that of pristine Co₃O₄. Then, the Gibbs free energy based on the LOM pathway was calculated. In this pathway, the oxygen vacancies are not pre-created in the established models because vacancy filling/lattice oxygen migration is involved in the LOM process. As exhibited in Fig. 6a–b and S41–S42,† the Ru site on Ru SAs–CoO_x cannot be an effective adsorption/desorption site for the LOM process owing to its too strong interaction with O*. In contrast, on the Co site, the largest change in free energy (not referred to as a potential-determining step due to step 4 being a chemical process without any charge transfer) is the formation of O₂ (step 4) and the corresponding free energy is 0.62 eV, significantly smaller than that of the AEM pathway without (1.04 eV)/with (1.42 eV) oxygen vacancies. It can be observed that the largest change in free energy of Ru SAs–CoO_x during the OER process is the formation of O₂, which is a chemical step without any charge transfer (Fig. S43–S44[†]). This finding was consistent with the Tafel slope analysis and suggested the presence of a mixed kinetic control mechanism.^{52,54} Furthermore, an advanced activity descriptor $G_{\text{max}}(\eta)$ was also utilized to comprehensively evaluate their activity trends. This descriptor identifies the largest free-energy span (uphill in free energy) among all intermediates within the catalytic process, considering both the electrochemical and chemical steps.^{72,73} As shown in Fig. S44,† when $U = 1.23\text{ V}$, the corresponding G_{max} for the LOM process (1.24 eV) is close to (less than 0.2 eV different from each other) that of the AEM process without oxygen vacancies (1.10 eV), while being smaller than that of the AEM process with oxygen vacancies (1.96 eV). Therefore, according to

these above theoretical results, we assume that the LOM mechanism is operational during the OER process on Ru SAs–CoO_x. However, the actual OER process is complex, so the triggering of the LOM process does not imply the elimination of the AEM process. The enhanced catalytic activity contributed to the synergistic effect of AEM and LOM. Considering that a small portion of Ru was substituted for the O_h site of Co₃O₄, the free energy diagrams for the OER on the Co and Ru site of Ru SAs–CoO_x (with Ru replacing O_h sites) based on the LOM were also calculated. The results showed that on the model of Ru SAs–CoO_x (with Ru replacing O_h sites), both the Ru (1.13 eV) and Co sites (1.33 eV) displayed a much higher energy barrier than the Co site of Ru SAs–CoO_x (with Ru replacing T_d sites). Therefore, the Co and Ru site of Ru SAs–CoO_x (with Ru replacing O_h sites) cannot be the effective adsorption/desorption site for the LOM process (Fig. S45–S47[†]).

In addition, considering that the OH* coverage on the catalyst surface in acidic media is comparatively low, the energy barrier for the H₂O-dissociation is calculated to offer a side reflection of OH* formation and coverage.⁷⁴ As shown in Fig. 6c and S48–S50,† the Co site on Ru SAs–CoO_x displays a much lower energy barrier (0.53 eV) for H₂O-dissociation compared to that of pristine Co₃O₄ (0.61 eV) as the Ru site improves the H₂O-dissociation ability on the Co site nearby and provides more OH* species for the lattice oxygen oxidation. Therefore, although Ru centers cannot be the effective adsorption/desorption site for OER processes, the significance of Ru should not be disregarded. Specifically, the active sites should be derived from the “Ru–O–Co” structural unit (Co: optimal adsorption/desorption sites. Ru: improve the H₂O-dissociation ability on the lattice oxygen site and provide plentiful OH* species for the subsequent oxidation process; increase the Co–O covalency and facilitate the direct O–O coupling. O: directly involved in O₂ evolution).

Additionally, an acknowledged drawback that DFT computations have limitations in describing the surface structure must be pointed out. In this study, only the (311) facet of Co₃O₄ was selected as the model, which simplified the complex structure of the Ru SAs–CoO_x electrocatalyst. In addition, the surface structure of the catalyst has changed during the OER process. However, the DFT simulations here still provide a wide understanding of why the electrocatalytic activity of Ru SAs–CoO_x improved compared with that of Co₃O₄.

To understand the enhanced durability of the prepared Ru SAs–CoO_x, the following two aspects were discussed. (1) Static durability: as displayed in Fig. 6d, the Co vacancy formation energy of T_d and O_h sites at Ru SAs–CoO_x (T_d: 0.80 eV and O_h: 2.43 eV) is higher than that of pristine Co₃O₄ (T_d: 0.11 eV and O_h: 2.18 eV), indicating a thermodynamically less favorable dissolution of Co from Ru SAs–CoO_x. Here, the Co vacancy formation energy is calculated at 0 K in a vacuum environment. The real experimental environment involves factors such as temperature, voltage, solvent, *etc.*, which makes it easier to produce vacancies in the actual environment. Therefore, although the DFT results indicate that Co vacancy formation energy of Ru SAs–CoO_x and pristine Co₃O₄ is not thermodynamically favorable (formation energy > 0), it can be inferred



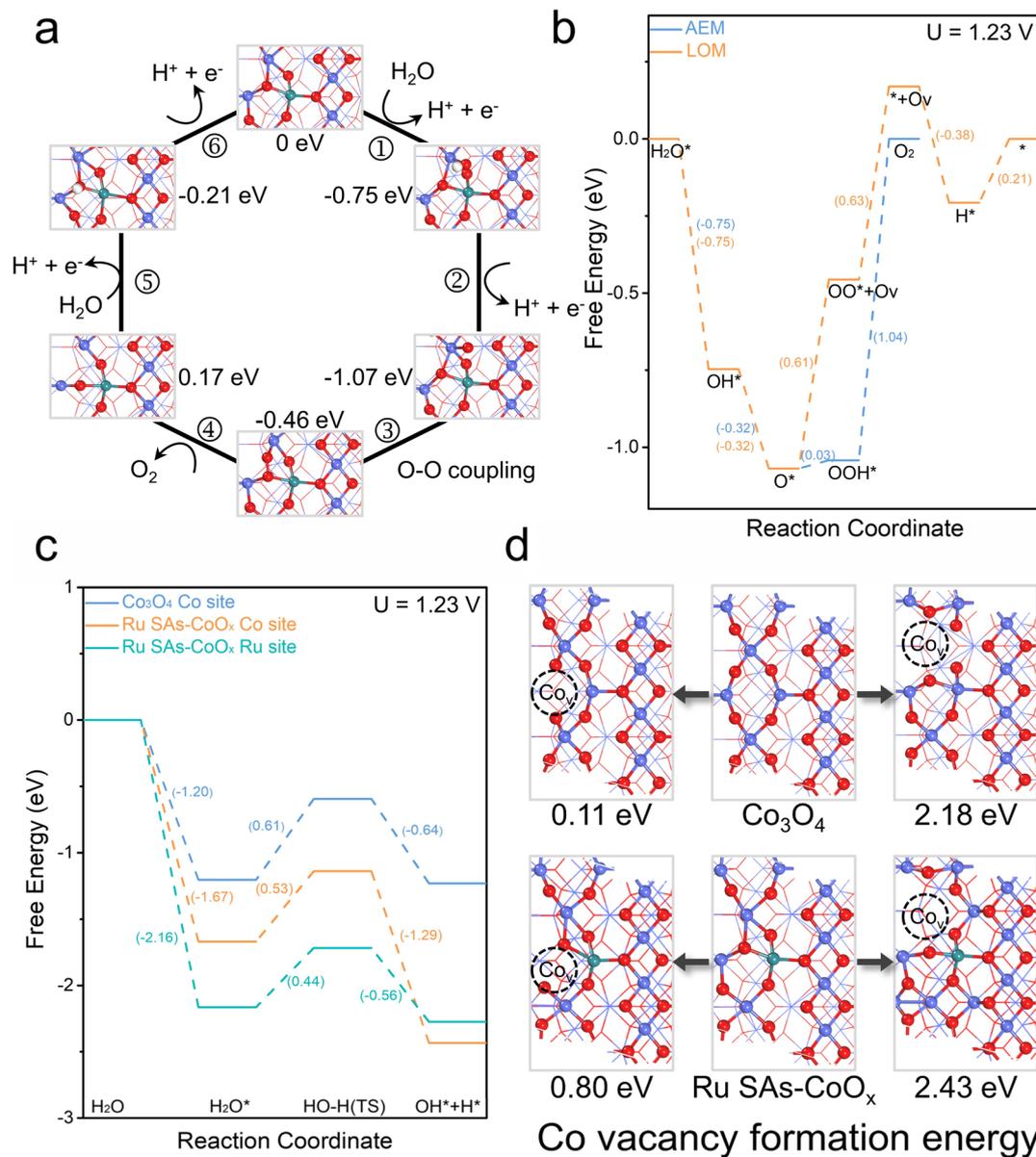


Fig. 6 Theoretical investigations. (a) Schematic illustration of the proposed OER mechanism based on the LOM process. (b) Calculated free energy diagrams for the OER on the Co site of Ru SAs-CoO_x (without oxygen vacancies) based on the AEM (corresponding to Fig. S34†) and LOM. (c) Calculated free energy diagram for H₂O-adsorption and H₂O-dissociation on different active sites. (d) Calculated Co vacancy formation energy on Co₃O₄ and Ru SAs-CoO_x.

from the trend of formation energy that the introduction of Ru enhances the static durability of Co. (2) Dynamic durability: direct O-O coupling mitigates the unstable reconstruction process before the formation of the OO bond, thereby extending the working lifetime of the electrocatalyst.

Conclusion

In this work, we reported a Ru SAs-CoO_x catalyst to overcome the balance between catalytic activity and dynamic durability for acidic OER *via* the preferential substitution of Ru for the Co²⁺ (T_d) site of Co₃O₄. Consequently, the overpotential at 10 mA cm⁻² of as-prepared Co₃O₄ (395 mV) sharply decreases to 188

mV by doping a small amount of Ru atoms (5.16 wt%), and its long-term durability is also prolonged. Combined with *in situ* measurement and DFT calculation, we hypothesized that the boosted activity and durability originated from the enhanced OH* coverage and Co-O covalency of Co₃O₄ after the introduction of Ru, which provided more OH* species for the OER process and mitigated the unstable reconstruction process. In addition, the obtained Ru SAs-CoO_x is superior to commercial RuO₂ and IrO₂ in price (1/3 of RuO₂ and 1/15 of IrO₂, respectively). We believe these findings will not only provide a guideline for the design of more efficient and stable catalysts but also pave a new avenue for the further exploration of the active site structure and catalytic mechanisms.



Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

J. Z., X. F., and H. S. conceived the project. J. Z. performed the experiments. G. C., D. S., Y. T. and W. X. offered help to analyze and discuss the experiment data. J. Z. wrote the manuscript. G. C., X. F., and H. S. gave helpful advice on the manuscript preparation. X. F. and H. S. co-supervised the project. All authors have approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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