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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 H<sub>2</sub> 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 Co<sub>3</sub>O<sub>4</sub> was effectively addressed *via* the preferential substitution of Ru for the Co<sup>2+</sup> (T<sub>d</sub>) site of Co<sub>3</sub>O<sub>4</sub>. *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<sub>x</sub> catalyst (5.16 wt% Ru) exhibits enhanced OER activity (188 mV overpotential at 10 mA cm<sup>-2</sup>) and durability, outperforming most reported Co<sub>3</sub>O<sub>4</sub>-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.<sup>1–7</sup> 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.<sup>8–10</sup> More importantly, the smaller gas crossover in acidic electrolyzers avoids the mixture of H<sub>2</sub> and O<sub>2</sub>, which ensures higher gas purity (note S1†).<sup>11,12</sup> 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 O<sub>2</sub> remains challenging in acidic media due to the scarcity of hydroxide anions (OH<sup>-</sup>), 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 Y<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub>,<sup>13</sup> bimetal oxide material (Li<sub>x</sub>RuO<sub>2</sub> and<sup>14</sup> Cr<sub>0.6</sub>Ru<sub>0.4</sub>O<sub>2</sub>,<sup>15</sup>), and perovskite-like material (SrTi<sub>1-x</sub>Ir<sub>x</sub>O<sub>3</sub> and<sup>16</sup> Sr<sub>2</sub>MIr(v)O<sub>6</sub>,<sup>17</sup>). However, the high cost and scarcity of noble metals limit their large-scale applications. Cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) 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 RuO<sub>2</sub>,<sup>18</sup> (2) remarkable static durability (resting state or open-circuit potential) in acidic media owing to the relatively strong overlapping of the octahedral Co<sup>3+</sup>(O<sub>h</sub>)–O orbital.<sup>19</sup> However, its practical catalytic performance in acidic media is not satisfactory: (1) compared that in alkaline media with abundant OH<sup>-</sup>, 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).<sup>20–22</sup> Thereby, to enhance the activity and durability of Co<sub>3</sub>O<sub>4</sub> 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.<sup>23–26</sup>

In order to facilitate the reaction pathway for direct O–O coupling, the moderate orbital overlap of metal–oxygen (M–O covalency) is essential.<sup>24,27,28</sup> 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 O<sub>2</sub>/H<sub>2</sub>O couple, which is thermodynamically favorable for the redox of lattice oxygen.<sup>29,30</sup> 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.<sup>5,31</sup> Therefore, we propose that moderate Co–O covalency of Co<sub>3</sub>O<sub>4</sub> 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<sub>x</sub>) 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;<sup>25</sup> (2) the introduction of Ru allows the enhanced orbital overlap between the Co 3d and O 2p, thus increasing the Co–O covalency;<sup>28</sup> (3) the doping of Ru promotes the generation of oxygen vacancies (O<sub>v</sub>), facilitating direct O–O coupling during the OER process and the oxygen evolution from lattice oxygen.<sup>19,32,33</sup> *In situ* <sup>18</sup>O 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<sub>x</sub> catalyst delivers a low overpotential of 188 mV at a current density of 10 mA cm<sup>-2</sup>, and enhanced long-term durability in acidic media, which are superior to those of pristine Co<sub>3</sub>O<sub>4</sub> (395 mV at 10 mA cm<sup>-2</sup>) and commercial RuO<sub>2</sub> (312 mV at 10 mA cm<sup>-2</sup>).

## 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<sub>x</sub>. To ascertain the doping position of Ru, we compared the formation energy for the substitution of tetrahedral Co<sup>2+</sup> (T<sub>d</sub>) and octahedral Co<sup>3+</sup> (O<sub>h</sub>) 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 Co<sup>2+</sup> (T<sub>d</sub>) with Ru leads to a lower barrier (1.194 eV) compared to that of the Co<sup>3+</sup>

(O<sub>h</sub>) site (2.803 eV), indicating a thermodynamically preferred replacement of Ru atoms at the Co<sup>2+</sup> (T<sub>d</sub>) site. Then, to evaluate the feasibility of the lattice oxygen oxidation reaction after Ru doping, the Co–O covalency and O<sub>v</sub> formation energy of Co<sub>3</sub>O<sub>4</sub> and Ru–Co<sub>3</sub>O<sub>4</sub> are calculated, respectively. As illustrated in Fig. 1a–c and Table S1,† the substitution of divalent tetrahedral Co<sup>2+</sup> (T<sub>d</sub>) with Ru<sup>3+</sup> 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.<sup>34,35</sup>

Besides, considering the crucial role of O<sub>v</sub> formation in facilitating direct O–O coupling, the O<sub>v</sub> formation energy in Co<sub>3</sub>O<sub>4</sub> and Ru–Co<sub>3</sub>O<sub>4</sub> is also calculated. The formation energies of four different types of O<sub>v</sub> in Co<sub>3</sub>O<sub>4</sub> are 1.509, 0.450, 2.863, and 2.820 eV, respectively (Fig. S4†). In the case of Ru–Co<sub>3</sub>O<sub>4</sub>, the corresponding formation energies for these four types of O<sub>v</sub> 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<sub>v</sub>. Therefore, the increased Co–O covalency and the lower O<sub>v</sub> 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).<sup>32,33</sup> 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<sub>x</sub> 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(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O 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 Co<sub>3</sub>O<sub>4</sub> nanoflower (Fig. S8c–d†). Subsequently, the Co<sub>3</sub>O<sub>4</sub> 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<sub>x</sub> sample was obtained after calcination at 300 °C, which could detach the chloride ligands and improve crystallization.<sup>36,37</sup>

X-ray diffraction (XRD) was employed to investigate the crystal structure of Co<sub>3</sub>O<sub>4</sub> and Ru SAs-CoO<sub>x</sub>. As depicted in Fig. 2b–c, the diffraction peaks of Co<sub>3</sub>O<sub>4</sub> were exhibited in the XRD pattern of Ru SAs-CoO<sub>x</sub>, and no diffraction peaks corresponding to Ru-related species could be detected, suggesting that the Ru species were highly dispersed or amorphous.<sup>38</sup> However, the incorporation of Ru<sup>3+</sup> with a larger ionic radius



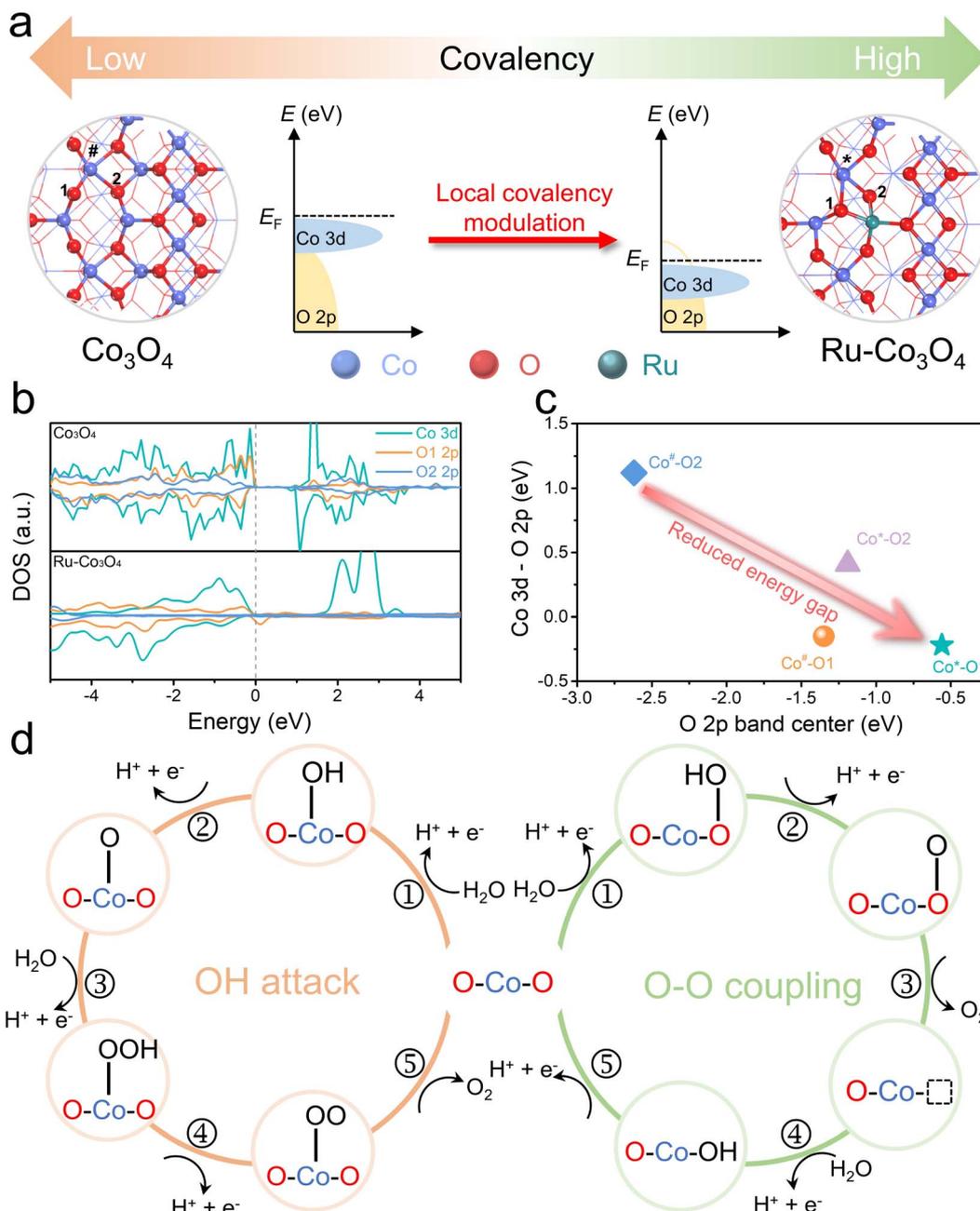


Fig. 1 Electronic structures and OER pathways. (a) Structures and schematic energy bands of  $\text{Co}_3\text{O}_4$  and  $\text{Ru-Co}_3\text{O}_4$  (the corresponding structure is shown in Fig. S5a†). (b) Computed DOS of Co 3d and O 2p for  $\text{Co}_3\text{O}_4$  and  $\text{Ru-Co}_3\text{O}_4$ . (c) Energy gap between Co 3d and O 2p versus the O 2p band center for  $\text{Co}_3\text{O}_4$  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  $\text{Co}_3\text{O}_4$  lattice. Consequently, Ru SAs- $\text{CoO}_x$  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  $\text{Co}_3\text{O}_4$ , which confirmed that the incorporation of Ru is not limited to the surface but extends into the  $\text{Co}_3\text{O}_4$  framework.<sup>38,39</sup> Besides, the broad peak observed between  $20^\circ$  and  $30^\circ$  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- $\text{CoO}_x$  were then examined

using transmission electron microscopy (TEM). As shown in Fig. 2d and S9–S10,† after introducing Ru atoms,  $\text{Co}_3\text{O}_4$  was transformed into the disordered nanosheet structure, where the interconnected nanostructures with certain amounts of holes could be observed. The  $\text{N}_2$  adsorption–desorption isotherms and the corresponding Brunauer–Emmett–Teller (BET) analysis showed that the surface area of Ru SAs- $\text{CoO}_x$  ( $155.46 \text{ m}^2 \text{ g}^{-1}$ ) was higher than that of pristine  $\text{Co}_3\text{O}_4$  ( $33.73 \text{ m}^2 \text{ g}^{-1}$ ), while the average pore size of Ru SAs- $\text{CoO}_x$  (4.41 nm) was found to be



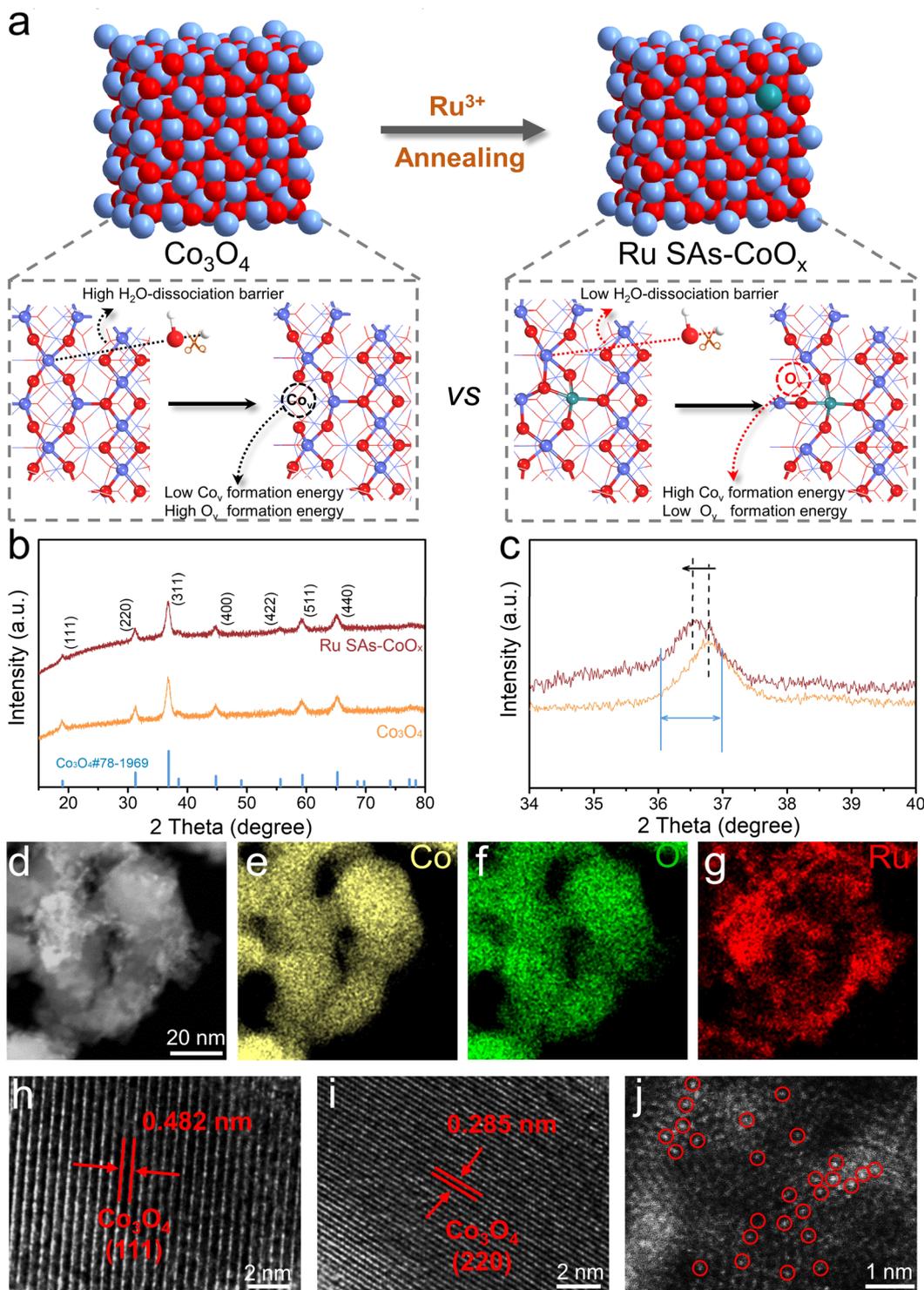


Fig. 2 Schematic illustration of the synthesis, mechanism, and morphological characterization studies. (a) The synthetic procedure and mechanism of Ru SAs- $\text{CoO}_x$  as an efficient electrocatalyst for acidic OER. (b) XRD patterns of Ru SAs- $\text{CoO}_x$  and  $\text{Co}_3\text{O}_4$  (ca.  $3^\circ \text{ min}^{-1}$ ). (c) Enlarged XRD pattern of Ru SAs- $\text{CoO}_x$  and  $\text{Co}_3\text{O}_4$ . (d–g) HAADF-STEM images of Ru SAs- $\text{CoO}_x$  and the corresponding elemental mapping images of Co, O, and Ru. (h and i) HRTEM images of Ru SAs- $\text{CoO}_x$ . (j) Atomic-resolution HAADF-STEM image of Ru SAs- $\text{CoO}_x$ . Ru atoms (marked by red circles) are uniformly distributed on the surface of  $\text{CoO}_x$ .

smaller compared with that of pristine  $\text{Co}_3\text{O}_4$  (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<sub>x</sub> 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 Co<sub>3</sub>O<sub>4</sub> (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<sub>x</sub>, confirming that Ru species were anchored on Co<sub>3</sub>O<sub>4</sub> in the form of single-atoms during the cation exchange process (Fig. 2j and S12†).<sup>40–42</sup>

Electron spin resonance (ESR) measurements were performed to investigate the generation of O<sub>v</sub>, and the signal corresponding to the electron trapped on O<sub>v</sub> was detected at  $g = 2.003$ . As shown in Fig. 3a, a stronger signal intensity of Ru SAs-CoO<sub>x</sub> was exhibited relative to pristine Co<sub>3</sub>O<sub>4</sub>, demonstrating

higher O<sub>v</sub> concentration.<sup>43</sup> To further substantiate the association between the increase in O<sub>v</sub> concentration and Ru doping, Ru-CoO<sub>x</sub> catalysts with different Ru contents were prepared by varying the dosage of Ru<sup>3+</sup> (*i.e.*, 0.025 mmol, 0.05 mmol, and 0.075 mmol). The resulting products were denoted as Ru-CoO<sub>x</sub>-0.025, Ru-CoO<sub>x</sub>-0.05, and Ru-CoO<sub>x</sub>-0.075 (*i.e.* Ru SAs-CoO<sub>x</sub>), respectively. The results of ESR also showed that the O<sub>v</sub> 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<sub>x</sub>, two major peaks located at 779.3 and 794.7 eV were assigned to Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub>, which were fitted by two regions of Co<sup>2+</sup> and Co<sup>3+</sup>. The relative atomic ratio of Co<sup>2+</sup>/Co<sup>3+</sup> could be obtained by comparing the area of the fitted curve. As more oxygen vacancies were generated on the surface of Ru SAs-CoO<sub>x</sub>, the ratio of Co<sup>2+</sup>/Co<sup>3+</sup> in Ru SAs-CoO<sub>x</sub> was expected to increase.<sup>44,45</sup> However, the ratio of Co<sup>2+</sup>/Co<sup>3+</sup> for the O<sub>v</sub>-rich Ru SAs-CoO<sub>x</sub>

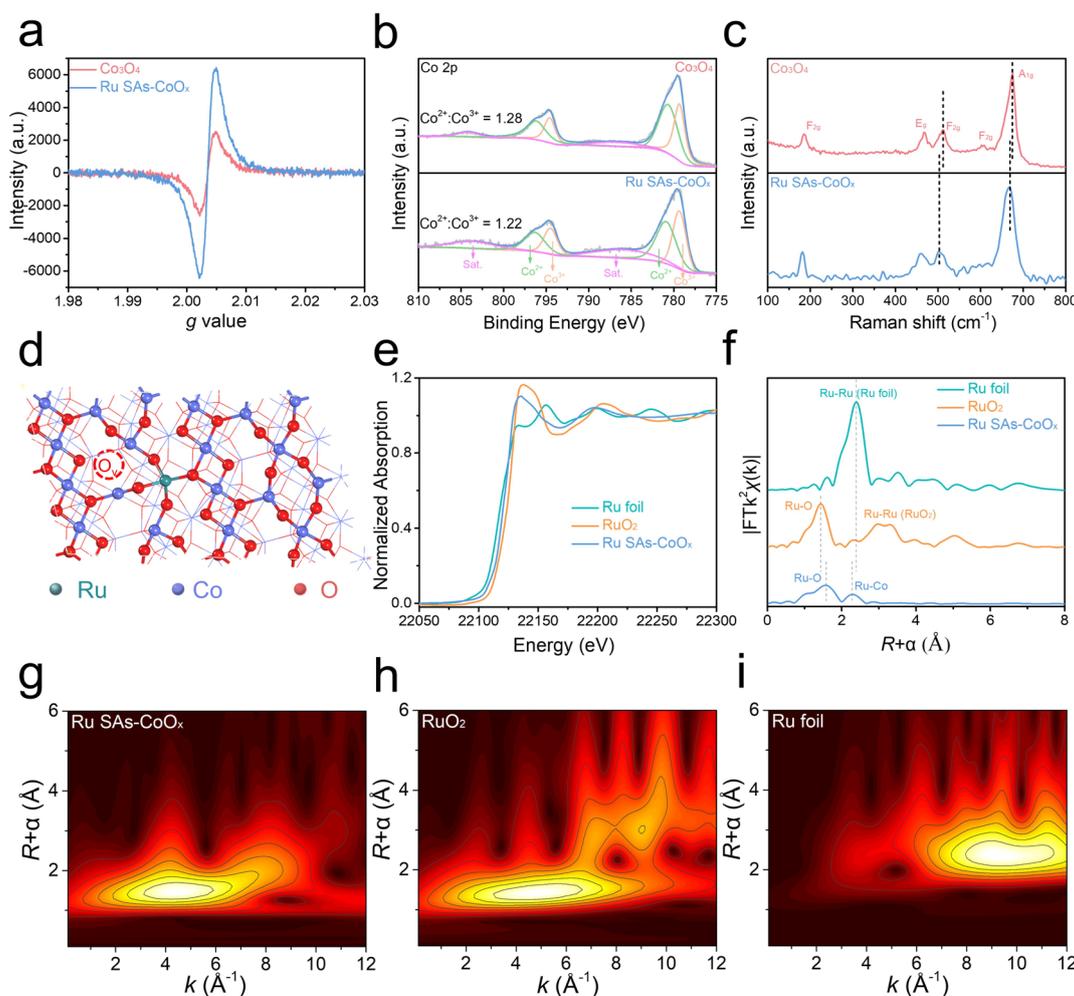


Fig. 3 Structure characterization of Ru SAs-CoO<sub>x</sub>. (a) ESR spectra of Ru SAs-CoO<sub>x</sub> and Co<sub>3</sub>O<sub>4</sub>. (b) Co 2p XPS spectra of Ru SAs-CoO<sub>x</sub> and Co<sub>3</sub>O<sub>4</sub>. (c) Raman spectra of Ru SAs-CoO<sub>x</sub> and Co<sub>3</sub>O<sub>4</sub>. (d) Structure of Ru SAs-CoO<sub>x</sub>. (e) Ru K-edge XANES spectra of Ru SAs-CoO<sub>x</sub>, Ru foil, and RuO<sub>2</sub>. (f) Fourier-transformed Ru K-edge EXAFS spectrum of Ru SAs-CoO<sub>x</sub>, Ru foil, and RuO<sub>2</sub>. (g–i) Wavelet transforms for the  $k^2$ -weighted Ru K-edge EXAFS signals of Ru SAs-CoO<sub>x</sub>, Ru foil, and RuO<sub>2</sub>.



(1.22) showed a slight decrease compared to that of the pristine  $\text{Co}_3\text{O}_4$  (1.28) (Fig. 3b), which indicated that the Ru atoms were doped into the  $\text{Co}_3\text{O}_4$  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- $\text{CoO}_x$  (1.22) showed a slight decrease compared to that of the pristine  $\text{Co}_3\text{O}_4$  (1.28), which suggested that Ru preferentially occupied  $T_d$  sites ( $\sim 78\%$ , note S2†).<sup>46,47</sup> In the Ru 3p spectrum (Fig. S14d†), the peaks of Ru 3p<sub>3/2</sub> and Ru 3p<sub>1/2</sub> located at 462.60 and 484.88 eV were detected, which are positioned between those of Ru (0) and Ru (iv),<sup>48</sup> demonstrating that the oxidation state of Ru in Ru SAS- $\text{CoO}_x$  was between 0 and +4 (Fig. S16†). Then Raman spectroscopy was conducted to reveal the structural changes in the coordination environment of  $\text{Co}_3\text{O}_4$ .<sup>49</sup> As shown in Fig. 3c, five characteristic peaks corresponding to the  $E_g$ ,  $F_{2g}$ , and  $A_{1g}$  of  $\text{Co}_3\text{O}_4$  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).<sup>49</sup> In order to investigate the local coordination of Ru species in Ru SAS- $\text{CoO}_x$ , the Ru *K*-edge region X-ray absorption near edge structure (XANES) was measured, which displayed clear differences from those of Ru foil and  $\text{RuO}_2$  (Fig. 3e). Extended X-ray absorption fine structure (EXAFS) for Ru SAS- $\text{CoO}_x$  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- $\text{CoO}_x$ . 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- $\text{CoO}_x$  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  $4.5\text{ Å}^{-1}$  (Ru–O scattering path) was detected in the WT contour plot of Ru SAS- $\text{CoO}_x$ . The signal corresponding to  $\text{Ru}_B\text{–O–Co}_B$  was not detected, which may be due to its weaker coordination.

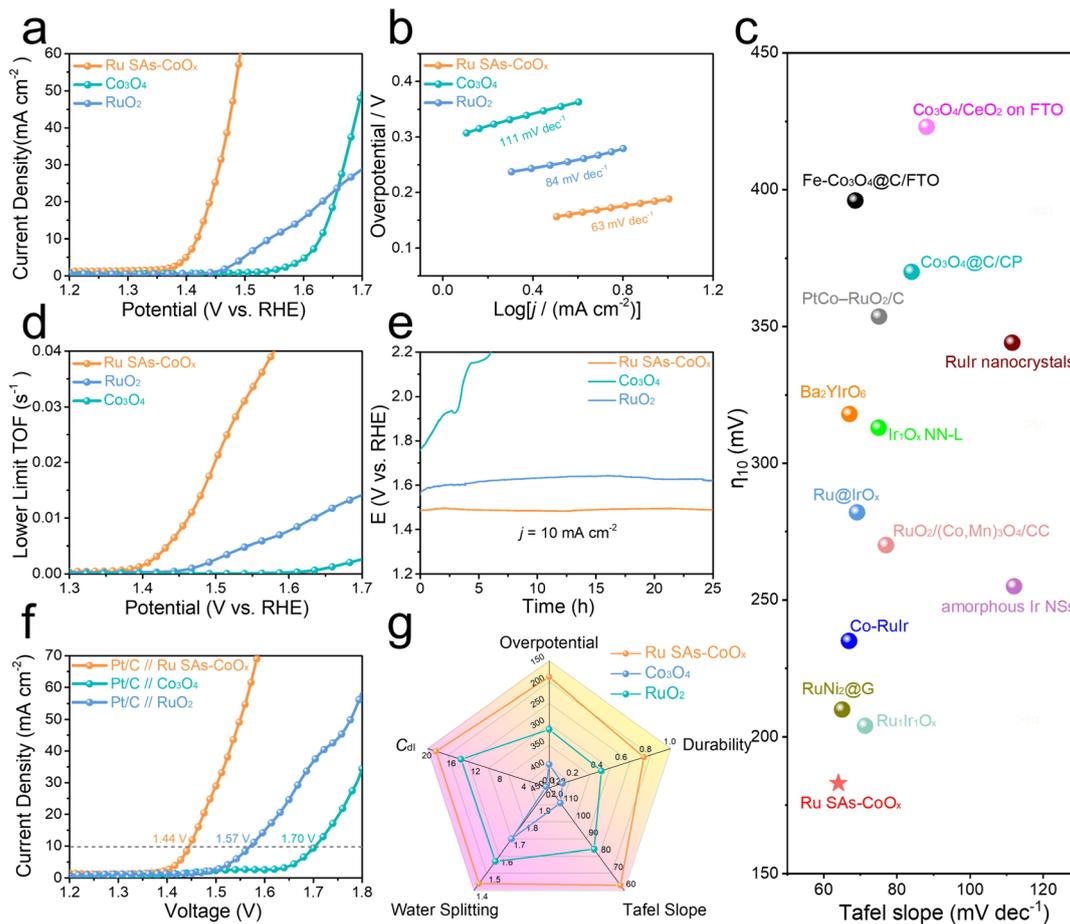
### Electrocatalytic performance of the OER in acidic media

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  $\text{N}_2$ -saturated 0.1 M  $\text{HClO}_4$  electrolyte were displayed. When the content of Ru reached 5.16 wt% (Fig. S18–S24 and Tables S3 and S4†) in the obtained Ru- $\text{CoO}_x$  (Ru SAS- $\text{CoO}_x$ ) catalyst, it showed a minimum overpotential of 188 mV at a current density of  $10\text{ mA cm}^{-2}$ , which was much smaller than that of commercial  $\text{RuO}_2$  (312 mV) and pristine  $\text{Co}_3\text{O}_4$  (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- $\text{CoO}_x$  was calculated to be  $63\text{ mV dec}^{-1}$ , which was much lower than that of pristine  $\text{Co}_3\text{O}_4$  ( $111\text{ mV dec}^{-1}$ ) and commercial  $\text{RuO}_2$  ( $84\text{ mV dec}^{-1}$ ), indicating the faster kinetics toward the OER.<sup>50,51</sup> 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.<sup>20,52–54</sup> Besides, several other points may also cause the value of the Tafel slope to deviate from  $60\text{ mV dec}^{-1}$  or  $120\text{ mV dec}^{-1}$ : (1) transfer coefficient ( $\alpha$ ) 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;<sup>†</sup> (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- $\text{CoO}_x$  also demonstrated its superior performance among  $\text{Co}_3\text{O}_4$ -based electrocatalysts, which is even well comparable with the reported Ir-based and Ru-based OER electrocatalysts in acidic media, such as Co–RuIr ( $235\text{ mV}$  at  $10\text{ mA cm}^{-2}$ ),<sup>55</sup> Ru@ $\text{IrO}_x$  ( $282\text{ mV}$  at  $10\text{ mA cm}^{-2}$ ),<sup>56</sup> amorphous  $\text{IrO}_2$  ( $255\text{ mV}$  at  $10\text{ mA cm}^{-2}$ ),<sup>57</sup>  $\text{Ba}_2\text{–YrIrO}_6$  ( $318\text{ mV}$  at  $10\text{ mA cm}^{-2}$ ),<sup>58</sup> Ir–STO ( $295\text{ mV}$  at  $10\text{ mA cm}^{-2}$ ),<sup>59</sup> and  $\text{RuNi}_2\text{@G-250}$  ( $210\text{ mV}$  at  $10\text{ mA cm}^{-2}$ )<sup>60</sup> (Fig. 4c and Table S5†). In addition, the exchange current density ( $j_0$ ) of Ru SAS- $\text{CoO}_x$  ( $0.033\text{ mA cm}^{-2}$ ) could be evaluated by extrapolating the Tafel slope (Fig. S25†), which was much higher than those of pristine  $\text{Co}_3\text{O}_4$  ( $0.004\text{ mA cm}^{-2}$ ) and commercial  $\text{RuO}_2$  ( $0.012\text{ mA cm}^{-2}$ ), demonstrating the fast electron transfer rate between the electrode and Ru SAS- $\text{CoO}_x$  catalyst surface.

We further investigated the electrochemical surface area (ECSA) of Ru SAS- $\text{CoO}_x$  by testing the double layer capacitances ( $C_{dl}$ ). Compared with those of pristine  $\text{Co}_3\text{O}_4$  ( $0.5\text{ mF cm}^{-2}$ ) and  $\text{RuO}_2$  ( $14.5\text{ mF cm}^{-2}$ ), the larger  $C_{dl}$  value ( $18.6\text{ mF cm}^{-2}$ ) 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  $\text{H}_2\text{O}$  dissociation, which benefited the generation of  $\text{OH}^*$  species, thereby facilitating the generation of abundant  $\text{OH}^*$  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.<sup>13,44,61</sup> 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- $\text{CoO}_x$  and  $\text{RuO}_2$  electrodes was estimated by making an approximation that all metal centers in the catalysts are available for the OER.<sup>62–64</sup> As displayed in Fig. 4d, the lower limit TOF value of Ru SAS- $\text{CoO}_x$  at 1.5 V is as high as  $0.02\text{ s}^{-1}$ , 7.7 times higher than that of  $\text{RuO}_2$ . 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<sub>x</sub>, Co<sub>3</sub>O<sub>4</sub>, and RuO<sub>2</sub>. (c) Comparison with the recently reported Ru-based, Ir-based, and Co-based OER electrocatalysts. (d) Lower limit TOF curves of Ru SAs-CoO<sub>x</sub>, Co<sub>3</sub>O<sub>4</sub>, and RuO<sub>2</sub>. (e) Chronopotentiometric curves of Ru SAs-CoO<sub>x</sub>, Co<sub>3</sub>O<sub>4</sub>, and RuO<sub>2</sub> recorded at a constant current density of 10 mA cm<sup>-2</sup>. (f) Polarization curves of the Pt/C//Ru SAs-CoO<sub>x</sub>, Pt/C//Co<sub>3</sub>O<sub>4</sub>, and Pt/C//RuO<sub>2</sub> electrolyzers for overall water splitting. (g) Comparison of overpotential (mV @ 10 mA cm<sup>-2</sup>), durability (current retention ratio), Tafel slope (mV dec<sup>-1</sup>), water splitting (mV @ 10 mA cm<sup>-2</sup>), and C<sub>dl</sub> (mF cm<sup>-2</sup>) for Ru SAs-CoO<sub>x</sub>, Co<sub>3</sub>O<sub>4</sub>, and RuO<sub>2</sub>.

faradaic efficiency of nearly 100% for the OER on Ru SAs-CoO<sub>x</sub> was evaluated by the water drainage method, indicating excellent selectivity for oxygen generation (Fig. S30<sup>†</sup>).

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<sup>-2</sup>. As revealed in Fig. 4e, Ru SAs-CoO<sub>x</sub> displayed a slight potential change from 1.485 to 1.494 V after 25 hours, which was far better than that of RuO<sub>2</sub> (1.556 V to 1.623 V, aligned with the trend of commercial RuO<sub>2</sub> in the reported literature studies.<sup>6,9</sup>) and pristine Co<sub>3</sub>O<sub>4</sub>. Meanwhile, the chronoamperometric curves of Ru SAs-CoO<sub>x</sub>, RuO<sub>2</sub> and pristine Co<sub>3</sub>O<sub>4</sub> were also recorded at the same initial current density (10 mA cm<sup>-2</sup>). The results indicated that the current retention of Ru SAs-CoO<sub>x</sub> after 20 hours was 77.3%, which was superior to RuO<sub>2</sub> (43.3%) and pristine Co<sub>3</sub>O<sub>4</sub> (10.6%) (Fig. S31<sup>†</sup>). Meanwhile, the durability of Ru SAs-CoO<sub>x</sub> was also compared with previously reported Co<sub>3</sub>O<sub>4</sub> electrocatalysts, which also exhibited a significantly better durability (Table S6<sup>†</sup>). After the durability test, the morphology, electronic structure, and composition of the catalysts were studied. As displayed in

Fig. S32–S34,<sup>†</sup> HRTEM and EDS results confirmed that the Ru SAs-CoO<sub>x</sub> 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.<sup>65,66</sup> The XRD pattern revealed that the Co<sub>3</sub>O<sub>4</sub> phase of Ru SAs-CoO<sub>x</sub> was well-maintained, although the peak intensity decreased obviously. This decrease was likely due to the surface composition of Ru SAs-CoO<sub>x</sub> 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<sup>-2</sup> in 0.1 M HClO<sub>4</sub> solution. The results, as indicated in Table S7,<sup>†</sup> revealed very low rates of Ru and Co dissociation.

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



mA cm<sup>-2</sup>) and Pt/C//Co<sub>3</sub>O<sub>4</sub> couple (1.70 V at 10 mA cm<sup>-2</sup>). To sum up, compared with pristine Co<sub>3</sub>O<sub>4</sub> and RuO<sub>2</sub>, Ru SAs-CoO<sub>x</sub> exhibited overwhelming advantages for the OER from the aspects of overpotential, Tafel slope, durability, water splitting, and C<sub>dl</sub> (Fig. 4g).

### Understanding the reaction mechanism

To rationalize the enhanced OER activity and durability of Ru SAs-CoO<sub>x</sub>, the reaction mechanism was explored. *In situ* <sup>18</sup>O 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 <sup>18</sup>O in the lattice and <sup>16</sup>O in the water,<sup>67</sup> confirming the successful <sup>18</sup>O labeling and the

involvement of the LOM during the OER process (Fig. S35†).<sup>34,68</sup> In contrast, the signals of <sup>34</sup>O<sub>2</sub> for pristine Co<sub>3</sub>O<sub>4</sub> were not detected, demonstrating that the low Co–O covalency and less O<sub>v</sub> concentration of Co<sub>3</sub>O<sub>4</sub> 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<sub>x</sub> during the OER process, *in situ* Raman spectroscopy was performed as well. Fig. 5c exhibits the Raman spectra of Ru SAs-CoO<sub>x</sub> recorded from 0 to 60 min at 1.5 V. Three characteristic peaks corresponding to the E<sub>g</sub> (~465 cm<sup>-1</sup>), F<sub>2g</sub> (~505 cm<sup>-1</sup>), and A<sub>1g</sub> (~660 cm<sup>-1</sup>) of Co<sub>3</sub>O<sub>4</sub> spinel oxides were detected. With the increase in the OER time, a new

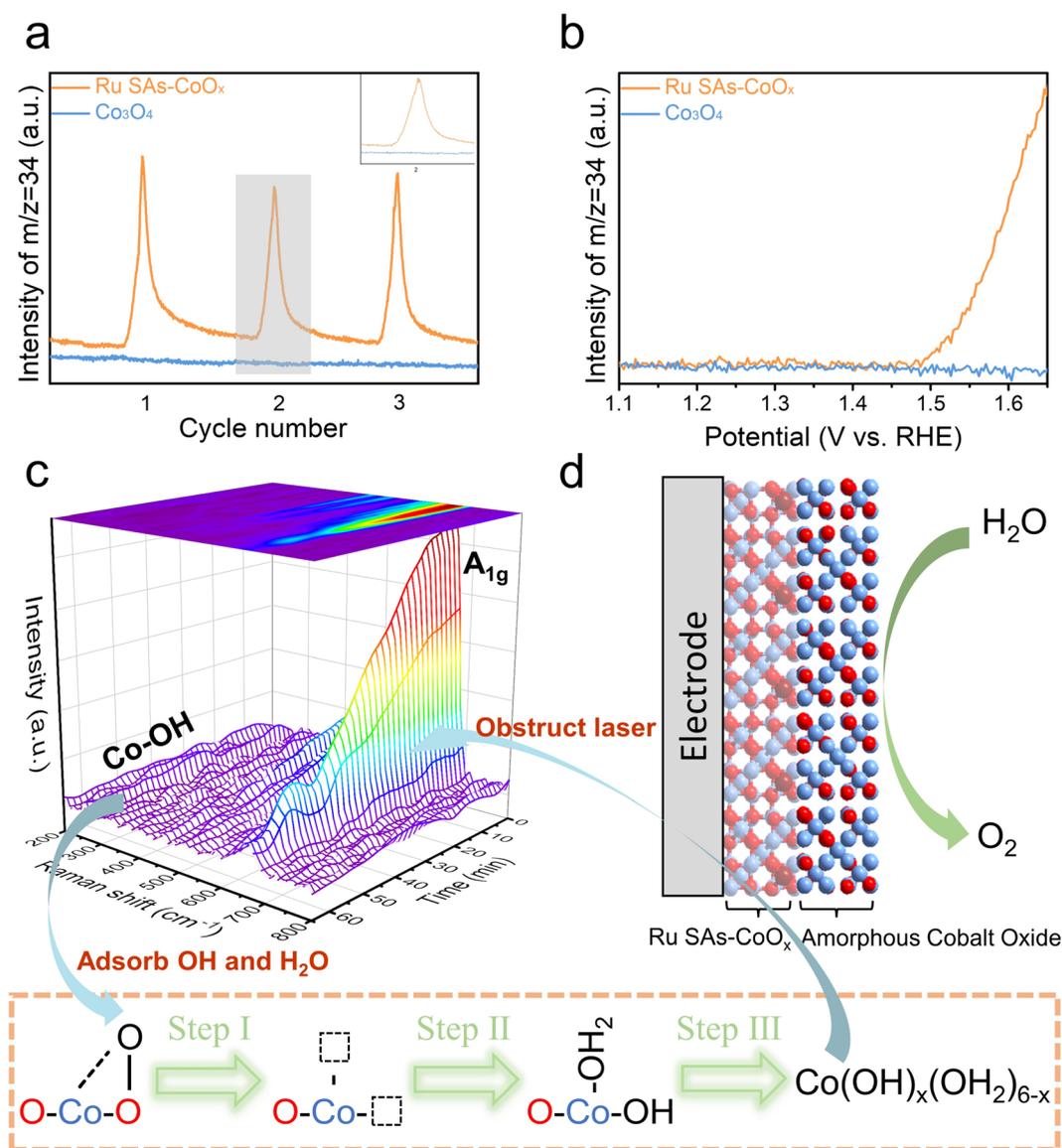


Fig. 5 Mechanism investigation of Ru SAs-CoO<sub>x</sub> during the OER process. (a) *In situ* DEMS signals of <sup>34</sup>O<sub>2</sub> for <sup>18</sup>O-labeled Ru SAs-CoO<sub>x</sub> and Co<sub>3</sub>O<sub>4</sub> in 0.1 M HClO<sub>4</sub> relative to time. (b) *In situ* DEMS signals of <sup>34</sup>O<sub>2</sub> for <sup>18</sup>O-labeled Ru SAs-CoO<sub>x</sub> and Co<sub>3</sub>O<sub>4</sub> in 0.1 M HClO<sub>4</sub> 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<sub>x</sub> 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<sup>†</sup>),<sup>69,70</sup> 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 H<sub>2</sub>O to form Co(OH)<sub>x</sub>(H<sub>2</sub>O)<sub>6–x</sub>, 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.<sup>19,71</sup> Based on the above results, although the durability was maintained well during the OER process, the surface structure of Ru SAs–CoO<sub>x</sub> 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<sub>x</sub>. 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 Co<sub>3</sub>O<sub>4</sub> and Ru SAs–CoO<sub>x</sub>. 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<sup>†</sup>). 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 Co<sub>3</sub>O<sub>4</sub>. This finding contradicts the observed enhanced catalytic activity of Ru SAs–CoO<sub>x</sub> compared to that of pristine Co<sub>3</sub>O<sub>4</sub>. 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<sub>x</sub> 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 O<sub>2</sub> (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<sub>x</sub> during the OER process is the formation of O<sub>2</sub>, which is a chemical step without any charge transfer (Fig. S43–S44<sup>†</sup>). This finding was consistent with the Tafel slope analysis and suggested the presence of a mixed kinetic control mechanism.<sup>52,54</sup> 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.<sup>72,73</sup> As shown in Fig. S44,† when  $U = 1.23\text{ V}$ , the corresponding  $G_{\text{max}}$  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<sub>x</sub>. 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<sub>h</sub> site of Co<sub>3</sub>O<sub>4</sub>, the free energy diagrams for the OER on the Co and Ru site of Ru SAs–CoO<sub>x</sub> (with Ru replacing O<sub>h</sub> sites) based on the LOM were also calculated. The results showed that on the model of Ru SAs–CoO<sub>x</sub> (with Ru replacing O<sub>h</sub> 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<sub>x</sub> (with Ru replacing T<sub>d</sub> sites). Therefore, the Co and Ru site of Ru SAs–CoO<sub>x</sub> (with Ru replacing O<sub>h</sub> sites) cannot be the effective adsorption/desorption site for the LOM process (Fig. S45–S47<sup>†</sup>).

In addition, considering that the OH\* coverage on the catalyst surface in acidic media is comparatively low, the energy barrier for the H<sub>2</sub>O-dissociation is calculated to offer a side reflection of OH\* formation and coverage.<sup>74</sup> As shown in Fig. 6c and S48–S50,† the Co site on Ru SAs–CoO<sub>x</sub> displays a much lower energy barrier (0.53 eV) for H<sub>2</sub>O-dissociation compared to that of pristine Co<sub>3</sub>O<sub>4</sub> (0.61 eV) as the Ru site improves the H<sub>2</sub>O-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 H<sub>2</sub>O-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 O<sub>2</sub> 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 Co<sub>3</sub>O<sub>4</sub> was selected as the model, which simplified the complex structure of the Ru SAs–CoO<sub>x</sub> 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<sub>x</sub> improved compared with that of Co<sub>3</sub>O<sub>4</sub>.

To understand the enhanced durability of the prepared Ru SAs–CoO<sub>x</sub>, the following two aspects were discussed. (1) Static durability: as displayed in Fig. 6d, the Co vacancy formation energy of T<sub>d</sub> and O<sub>h</sub> sites at Ru SAs–CoO<sub>x</sub> (T<sub>d</sub>: 0.80 eV and O<sub>h</sub>: 2.43 eV) is higher than that of pristine Co<sub>3</sub>O<sub>4</sub> (T<sub>d</sub>: 0.11 eV and O<sub>h</sub>: 2.18 eV), indicating a thermodynamically less favorable dissolution of Co from Ru SAs–CoO<sub>x</sub>. 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<sub>x</sub> and pristine Co<sub>3</sub>O<sub>4</sub> is not thermodynamically favorable (formation energy > 0), it can be inferred



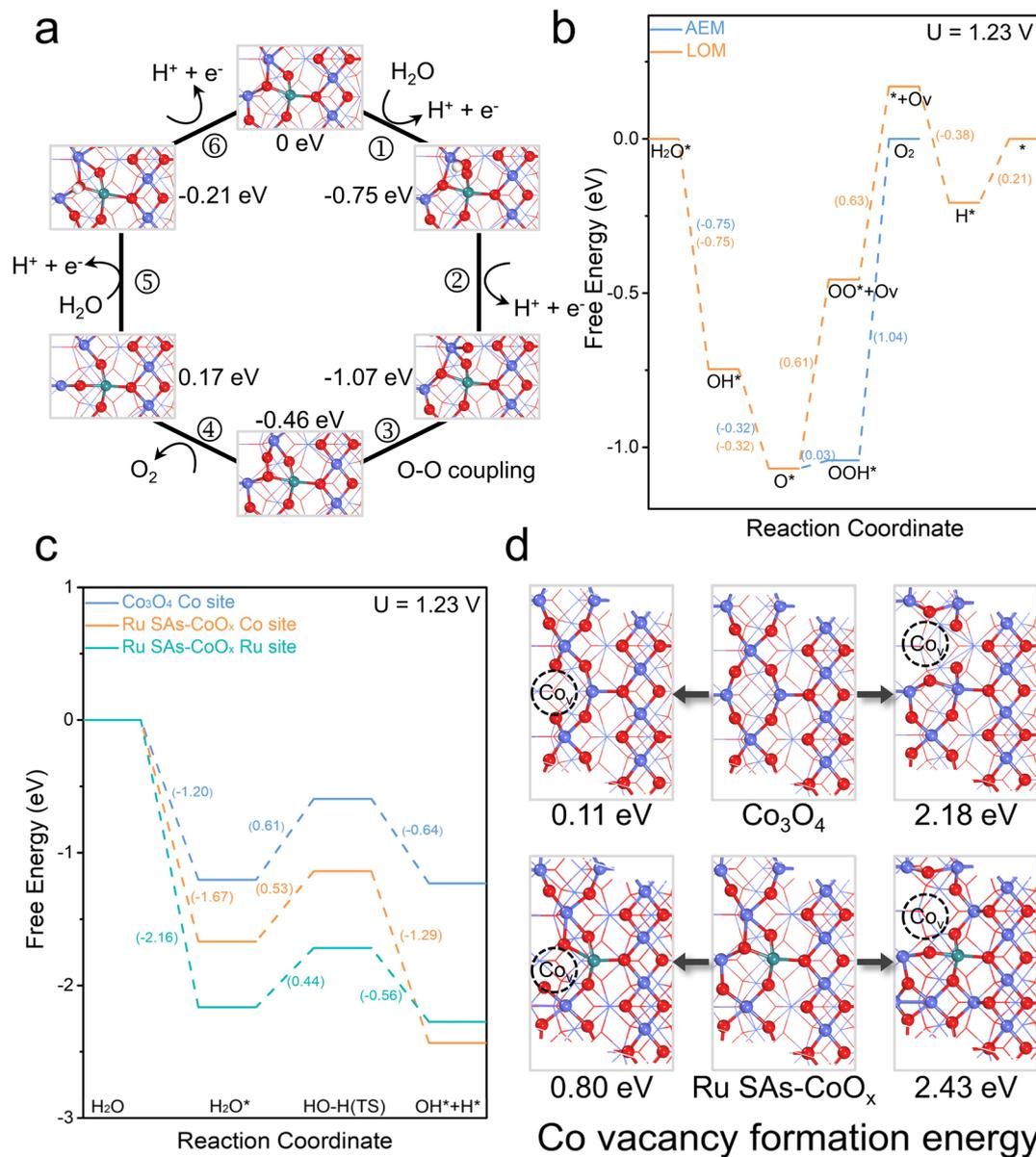


Fig. 6 Theoretical investigations. (a) Schematic illustration of the proposed OER mechanism based on the LOM process. (b) Calculated free energy diagrams for the OER on the Co site of Ru SAs-CoO<sub>x</sub> (without oxygen vacancies) based on the AEM (corresponding to Fig. S34†) and LOM. (c) Calculated free energy diagram for H<sub>2</sub>O-adsorption and H<sub>2</sub>O-dissociation on different active sites. (d) Calculated Co vacancy formation energy on Co<sub>3</sub>O<sub>4</sub> and Ru SAs-CoO<sub>x</sub>.

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<sub>x</sub> catalyst to overcome the balance between catalytic activity and dynamic durability for acidic OER *via* the preferential substitution of Ru for the Co<sup>2+</sup> (T<sub>d</sub>) site of Co<sub>3</sub>O<sub>4</sub>. Consequently, the overpotential at 10 mA cm<sup>-2</sup> of as-prepared Co<sub>3</sub>O<sub>4</sub> (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 Co<sub>3</sub>O<sub>4</sub> 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<sub>x</sub> is superior to commercial RuO<sub>2</sub> and IrO<sub>2</sub> in price (1/3 of RuO<sub>2</sub> and 1/15 of IrO<sub>2</sub>, 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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