

Tracking the correlation between spintronic structure and oxygen evolution reaction mechanism of cobalt-ruthenium-based electrocatalyst

Received: 23 May 2024

Accepted: 23 December 2024

Published online: 02 January 2025



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Regulating the spintronic structure of electrocatalysts can improve the oxygen evolution reaction performance efficiently. Nonetheless, the effects of tuning the spintronic structure for the oxygen evolution reaction mechanisms have rarely been discussed. Here, we show a ruthenium-cobalt-tin oxide with optimized spintronic structure due to the quantum spin interaction of Ru and Co. The specific spintronic structure of ruthenium-cobalt-tin oxide promotes the charge transfer kinetics and intermediates evolution behavior under applied potential, generating long-lived active species with higher spin density sites for the oxygen evolution reaction after the reconstruction process. Moreover, the ruthenium-cobalt-tin oxide possesses decoupled proton-electron transfer procedure during the oxygen evolution reaction process, demonstrating that the electron transfer procedure of O-O bond formation between *O intermediate and lattice oxygen in Co-O-Ru is the rate-determining step of the oxygen evolution reaction process. This work provides rational perspectives on the correlation between spintronic structure and oxygen evolution reaction mechanism.

The industrial revolutions have introduced advanced technology to affect the lifestyle of human beings¹. Behind the boom are environmental deterioration and energy crises due to the extreme dependence on fossil fuels. To date, considerable efforts have been devoted to developing sustainable methods to yield renewable fuel^{2–4}. Electrochemistry technology is an efficient way to produce green value-added products, because of its fast reaction rates, optimized transformation efficiency, and high selectivity^{5–7}. In particular, the oxygen

evolution reaction (OER) is crucial for extending electrochemistry technology and plays an indispensable role in supplying protons and balancing charge. Generally, the OER involves a complex process which includes electron transfer, cleavage of O-H and O-O formation, resulting in a sluggish kinetics process^{8,9}. The development of appropriate electrocatalysts has been attracted more attentions^{8–12}. Therefore, the pivotal task is to design OER electrocatalysts with high efficiency and low cost.

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OER activity is always influenced by the characteristics of electrocatalysts, such as crystallinity, morphology, and electronic structure, etc.^{12,13}. Establishing structure-activity correlations as hotspots can provide criteria for the design of OER electrocatalysts¹⁴. For instance, Shao-Horn's group reported that perovskite oxides with optimized e_g occupancy could act as superior OER catalysts¹⁵. Currently, exploring the relationship between the spintronic structure of a catalyst and its OER performance causes great concerns. The OER process suffers sluggish spin-state transitions of reaction intermediates, resulting in slow kinetics. In this respect, specific spintronic configurations of electrocatalysts could regulate the spin-oriented electrons of intermediates, impairing obstacles caused by sluggish spin-state transitions¹⁶. However, the pristine electrocatalysts usually suffer structural reconstruction during the OER process, forming active species with rational structures for efficient reaction kinetics^{13,17}. The reconstruction process was always ignored when the spintronic structure-activity relationship was considered. Thus, identifying the complicated relationships among the spintronic structure, surface reconstruction, and OER mechanisms is inevitable but challenging.

Owing to the complex spintronic structure and reconstruction process of electrocatalysts, the OER mechanisms are intricate. Elucidating the practical OER process is essential. Generally, electrochemical reactions include electron transfer and intermediates evolution, resulting in a proton-coupled electron transfer (PCET) process¹⁸. OER is regarded as a concerted proton-coupled electron transfer (CPET), which acquiescently occurs at a steady surface¹⁹. However, the dynamic reconstruction of OER electrocatalysts always occurs, providing the possibility for decoupled proton and electron transfer reactions (DPET) during the OER²⁰. Thus, it brings difficult to trace the OER process because more factors need to be considered (such as charge transfer, reconstruction of electrocatalysts and intermediates evolution, etc)^{21–24}. To date, there are few reports on the comprehensive understanding of the mechanisms involved, tracing the practical OER process by the kinetic features of electrocatalysts.

Herein, a ruthenium-cobalt-tin oxide (A-RSCOH) as a superior OER electrocatalyst is reported. From the vibrating sample magnetometer, the quantum spin interactions of Ru and Co optimize the spintronic structure of A-RSCOH, which promotes the A-RSCOH to act as a spin channel for spin-oriented electron transfer. The in situ electrochemical spectroscopy and electrochemical kinetic measurements reveal the favorable charge transfer kinetics and intermediates evolution behavior under applied potential while capturing long-lived active species with higher spin density sites generated from the reconstruction process. Moreover, the comprehensive experimental and theoretical results demonstrate the existence of the DPET procedure during the OER process, and the rate-determining step is the electron transfer of O-O bond formation between the *O intermediate and lattice oxygen in Co-O-Ru. This work provides prospective perceptions of practical OER mechanisms and the design of outstanding OER electrocatalysts.

Results

Electrocatalyst synthesis and characterization

Generally, surface reconstruction usually occurs on pre-catalysts, resulting in a kinetically stable state of the electrocatalysts. It is of great significance to track the structure-activity correlations of stable catalysts. Thus, the crystal structure and morphology of cobalt-based catalysts were explored. Typically, the amorphous RuSnCoOH (labeled as A-RSCOH) was prepared by doping Ru into amorphous SnCoOH (labeled as A-SCOH) via an ion exchange-pyrolysis method. Prior to obtaining A-SCOH, the $SnCo(OH)_6$ (labeled as SCOH) was fabricated via a co-precipitation process. The X-ray diffraction (XRD) pattern is shown in Supplementary Fig. 1, and the representative peaks of SCOH are attributed to the perovskite-type cobalt-tin hydroxide (JCPDS: 13-0356)²⁵. After calcining under a reducing atmosphere, the characteristic peaks of $SnCo(OH)_6$ disappear, indicating the amorphous

structure of A-SCOH. In addition, the amorphous structure is maintained after doping of Ru, and no other XRD peaks appear.

The morphology of the as-prepared electrocatalysts was characterized by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). Numerous accumulations of SCOH nanocubes are observed in the SEM images, and this is maintained for A-SCOH and A-RSCOH (Supplementary Figs. 2–7 and Fig. 1a). From the TEM images in Supplementary Figs. 8–12, the shape of the nanocube morphology for A-SCOH becomes softened compared with the pristine SCOH, while no obvious difference between A-SCOH and A-RSCOH is discovered (Fig. 1bc). The high-resolution transmission electron microscopy (HR-TEM) images confirmed the amorphous structure of A-SCOH and A-RSCOH (Fig. 1d and Supplementary Figs. 10, 12). For the distinct lattice fringe in Supplementary Fig. 8, the lattice distance of 0.234 nm for SCOH can be indexed to the (311) facet, in accordance with the XRD patterns. Furthermore, the energy-dispersive spectroscopy (EDS) elemental mapping of SCOH, A-SCOH, and A-RSCOH are shown in Supplementary Figs. 1–11 and Fig. 1e, revealing that each element is distributed homogeneously in the nanocubes.

The chemical composition and electronic structure of the catalysts in the near-surface were investigated by X-ray photoelectron spectroscopy (XPS). The XPS peaks at 781.3 ($2p_{3/2}$) and 796.8 eV ($2p_{1/2}$) with satellite peaks of A-RSCOH are shown in Supplementary Fig. 14a, corresponding to the Co^{2+26} . In addition, two XPS peaks at 780.1 and 795.9 eV emerged, which are ascribed to Co^{3+} . According to the high-resolution XPS spectrum of Sn $3d$, the peak for Sn $3d_{5/2}$ (486.6 eV) of A-RSCOH is attributed to the Sn^{4+} (Supplementary Fig. 14b). The O 1s XPS peak split into three peaks located at 529.8, 531.1 and 532.5 eV, which are attributed to metal-oxygen (M-O), metal-hydroxyl (M-OH) and adsorbed H_2O , respectively (Supplementary Fig. 14d). The Ru $3p_{3/2}$ spectra are deconvoluted into the peaks at 463.7 and 466.4 eV, indicating that the valence state of Ru in A-RSCOH is the mixture of +3 and +4 (Supplementary Fig. 14c)^{27,28}. For the A-RSCOH, the Co $2p$ peaks shift positively in comparison to the XPS of A-SCOH, indicating that the doping of Ru induces electronic coupling to promote charge density redistribution. The XPS spectra of SCOH and A-SCOH are shown in Supplementary Figs. 13 and 14 for comparison.

The X-ray absorption spectroscopy (XAS) was conducted on A-RSCOH and A-SCOH to explore the electronic structure and coordination information. X-ray absorption near-edge structure (XANES) spectra of the Ru K-edge are shown in Supplementary Fig. 15a, which presents the chemical states of Ru in A-RSCOH. It is observed clearly that the pre-edge and white line peaks are similar to RuO_2 , demonstrating the valence state of Ru in A-RSCOH is approximately +4²⁹. From the analysis of the Fourier transform extended X-ray absorption fine structure (EXAFS) spectroscopy of A-RSCOH in Supplementary Fig. 15, a first shell at 1.52 Å of Ru-O is discovered. No characteristic coordination information of the Ru-Ru bond is observed. This coordination environment of Ru in A-RSCOH was further verified by wavelet transforms EXAFS (WT-EXAFS) (Supplementary Fig. 16). From the XANES spectra at the Co K-edge, the adsorption edges of A-SCOH and A-RSCOH are located between the Co foil and Co_3O_4 and are similar to $Co(OH)_2$ (Fig. 1f), indicating that the average valence state of Co is close to +2. The EXAFS peaks at 1.46 Å are observed in Fig. 1g, corresponding to the first-shell Co-O scattering, which are further proven in WT-EXAFS (Fig. 1i–l)³⁰. In addition, the pre-edge of Co K-edge at 7710 eV represents the transition of $1s \rightarrow 3d$, reflecting the symmetry of the coordination structure³¹. The pre-edge of A-SCOH and A-RSCOH are similar to $Co(OH)_2$ and $CoOOH$, indicating that the local coordinations of A-SCOH and A-RSCOH are similar to those of $Co(OH)_2$ and $CoOOH$. Furthermore, the local coordination of A-SCOH and A-RSCOH was further investigated by combining the detailed structural parameters through quantitative fitting of EXAFS spectra (Fig. 1h and Supplementary Fig. 17), and the average coordinative numbers (CN) of

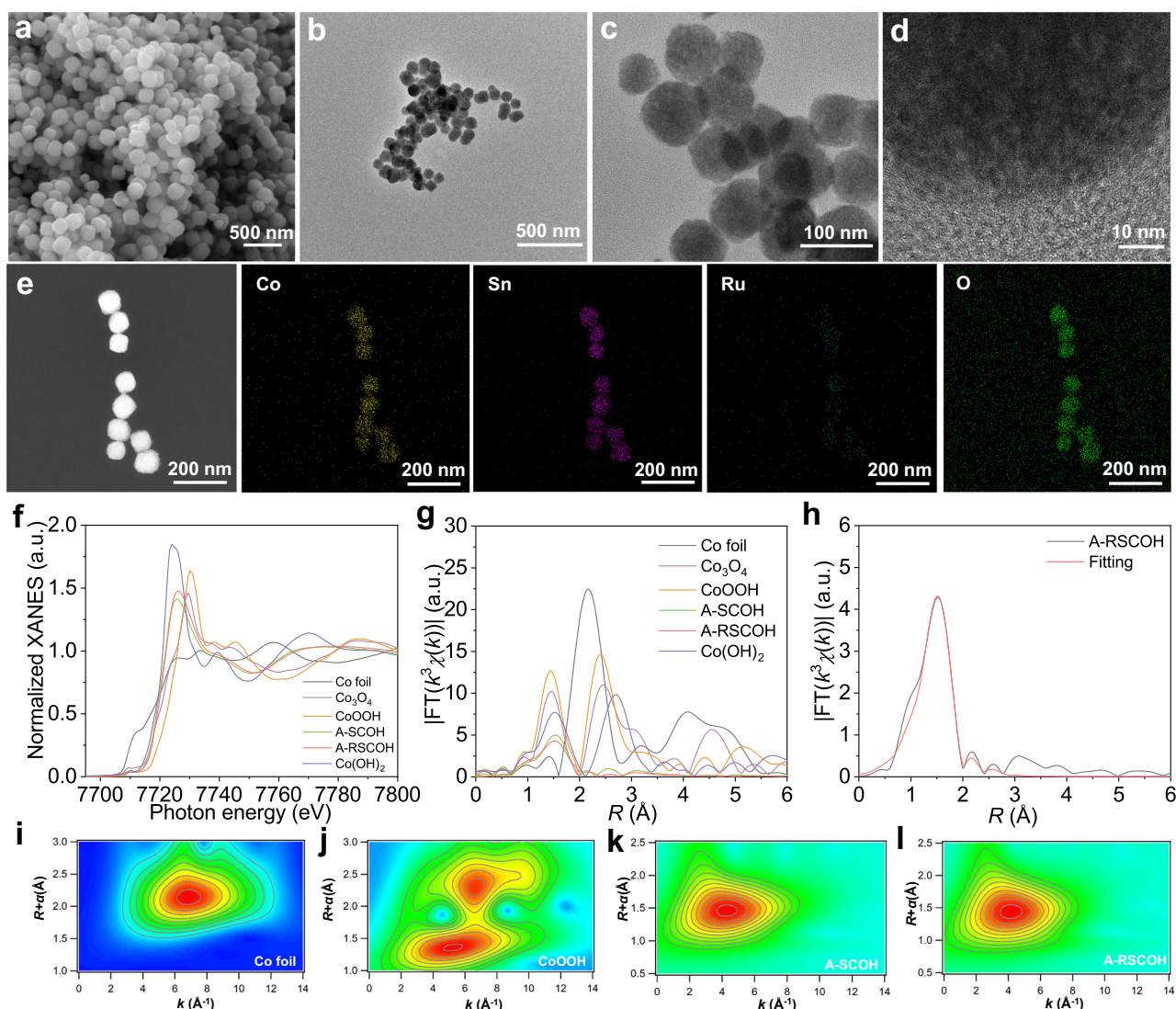


Fig. 1 | Morphology and structural characterizations of as-prepared pre-catalysts. **a** SEM, **(b, c)** TEM, **(d)** HR-TEM images of A-RSCOH. **e** HADDF-STEM image and element mapping of A-RSCOH. **f, g** XANES (**f**) and FT-EXAFS (**g**) at Co K-edge of as-prepared electrocatalysts. **h** FT-EXAFS and relevant fitting curves of A-RSCOH.

i–l WT-EXAFS (the R in ordinate and k in abscissa represent the distance from the central atom and the wavelength of the oscillation) of Co foil (**i**), CoOOH (**j**), A-SCOH (**k**), A-RSCOH (**l**).

Co–O and Ru–O in A-SCOH and A-RSCOH are around 5 (Supplementary Table 1).

The electron spin and orbital interactions are closely associated with the behavior of electrocatalysts during OER^{32,33}. The physical property measurement system (PPMS) was employed to explore the magnetic properties and spin structure. The magnetic moment of pre-catalysts was recorded from 0 to 300 K under a field-cooling pattern at a magnetic field of $H = 1000$ Oe. The magnetic susceptibilities (χ) were plotted against the temperature derived from temperature-dependent magnetization curves and obeyed paramagnetic Curie–Weiss law in the high-temperature region³⁴. The temperature-dependent magnetization curves present visible differences, indicating the variations in the spin structures of the as-prepared samples (Fig. 2a,b and Supplementary Figs. 18,19). The effective magnetic moment (μ_{eff}) of electrocatalysts, which can reflect the unpaired d electrons according to the equation presented in Supplementary Note 1, is generated from the curves in Fig. 2a,b and Supplementary Figs. 18, 19. Compared with SCOH and A-SCOH, the obvious increase in μ_{eff} for A-RSCOH reflects an increase in the number of unpaired d electrons, demonstrating the quantum spin interaction of Ru and Co. The models of A-SCOH and

A-RSCOH generated from molecular dynamics (MD) are shown in Fig. 2c and Supplementary Fig. 20, the variation trend of the calculated magnetic moment is consistent with the experimental results. The density of state (DOS) of A-SCOH and A-RSCOH are shown in Fig. 2d and Supplementary Figs. 21, 22, the introduction of Ru improves the DOS around Fermi level, indicating that the quantum spin interaction of Ru and Co improve the electron transfer ability³⁵.

Influence of spintronic structure on pre-catalysts reconstruction

Owing to the ‘electrochromicity’ of metal oxides, operando UV–Vis spectroscopy (Supplementary Note 2) was employed to trace the variations in the oxidation state of active metal sites^{36,37}. A distinct optical feature emerges for all the samples, after immersion in 1 M KOH (Supplementary Figs. 23–25), indicating that the structure of the electrocatalyst varied due to solvation. The potential was applied after all the electrocatalysts were stabilized in the electrolyte. A broad peak centered at approximately 420 nm emerges for A-RSCOH at 0.9 V, which is attributed to the oxidation of Co^{2+} to Co^{3+} (Fig. 2e). A similar optical feature according to the oxidation from Co^{2+} to Co^{3+} for SCOH

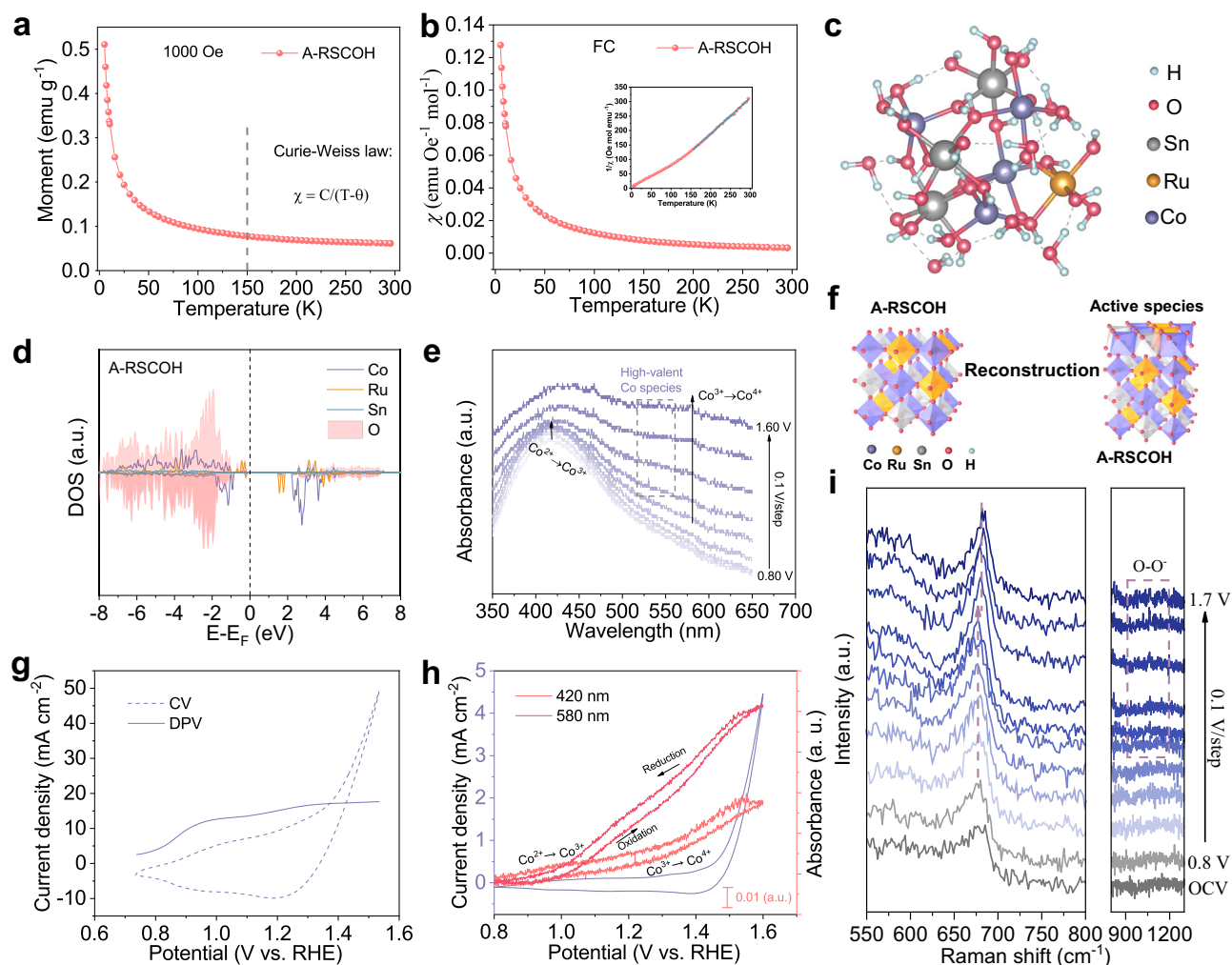


Fig. 2 | Influence of spintronic on pre-catalysts reconstruction. **a** Field cooling curve of A-RSCOH at 1000 Oe. **b** Variations of magnetization (χ) vs. temperature and the corresponding fitted curve are shown in the inserted pattern. **c** The model of A-RSCOH generated from MD simulations. **d** The projected density of state (pDOS) of Co, O, Ru, and Sn orbitals in A-RSCOH. **e** Operando UV-Vis adsorption

spectra of A-RSCOH at different potentials. **f** Schematic of reconstruction for A-RSCOH. **g** CV and DPV curves of A-RSCOH (without iR compensation). **h** UV-Vis absorbance variations along with CV measurement and relevant CV curve. **i** In situ Raman spectra of A-RSCOH at different potentials.

and A-SCOH is observed when the applied potential up to 1.0 V. For A-RSCOH, another increase in absorbance at approximately 580 nm is observed at 1.20 V and above, which is attributed to the process of $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$. For SCOH and A-SCOH, the characteristic absorption band of $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$ emerges at 1.3 V and above. Moreover, an obvious optical feature of A-RSCOH at approximately 525 nm appears at 1.3 V and above, corresponding to the accumulation of high-valent Co species³⁶ (Fig. 2e). The UV-Vis absorbance changes at 420 and 580 nm with cyclic voltammetry (CV) potentials ranging from 0.8 to 1.6 V were recorded through the kinetic module. The UV-Vis absorbance variations are consistent with the CV curves (Fig. 2h), indicating that both $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ and $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$ processes for A-RSCOH occur at lower applied potential than those of SCOH and A-SCOH. Obviously, adsorbed oxygenated intermediates in the reaction system must participate in these redox transitions. Lower driving potential for A-RSCOH results in a lower thermodynamic driving force for the utilization of adsorbed oxygenated intermediates, which accelerate the reconstruction process to produce active species of the OER. The reconstruction process of electrocatalysts is further explored by electrochemical kinetics characterization.

The Raman spectra of pristine A-SCOH and A-RSCOH have two Raman peaks at 510 and 623 cm^{-1} , which are the characteristic peaks of Co-O and Co-OH bonds³⁸, respectively (Supplementary Fig. 26a and 28a). The in-situ Raman spectra of A-SCOH and A-RSCOH are shown in Supplementary Figs. 26–29 and Fig. 2i, revealing the evolution of electrocatalysts under applied potential (Supplementary Note 3). The structures of A-SCOH and A-RSCOH transformed after immersion in 1 M KOH, which was induced by solvation at the open circuit voltage (OCV). The peaks at approximately 508, 602 and 674 cm^{-1} are visible in Supplementary Figs. 26–29, and are attributed to the vibrational modes of Co-O, which are typical of amorphous CoOOH ³⁹. There are no changes in the Raman bands at 0.8 V. The Raman bands of A-RSCOH shift along with the applied potential up to 0.9 V. Combined with in situ UV-Vis spectra, CV and differential pulse voltammetry (DPV) curves (Fig. 2g), the oxidation from Co^{2+} to Co^{3+} starts at 0.9 V and completes at 1.1 V and above. Thus, the Raman shift between 0.9 and 1.1 V reflects the transformation of Co^{2+} species into CoOOH . These Raman bands gradually shift at 1.2 V and above, indicating another phase transformation process. In addition, the Raman bands stabilize at ~487, 572 and 680 cm^{-1} when the applied

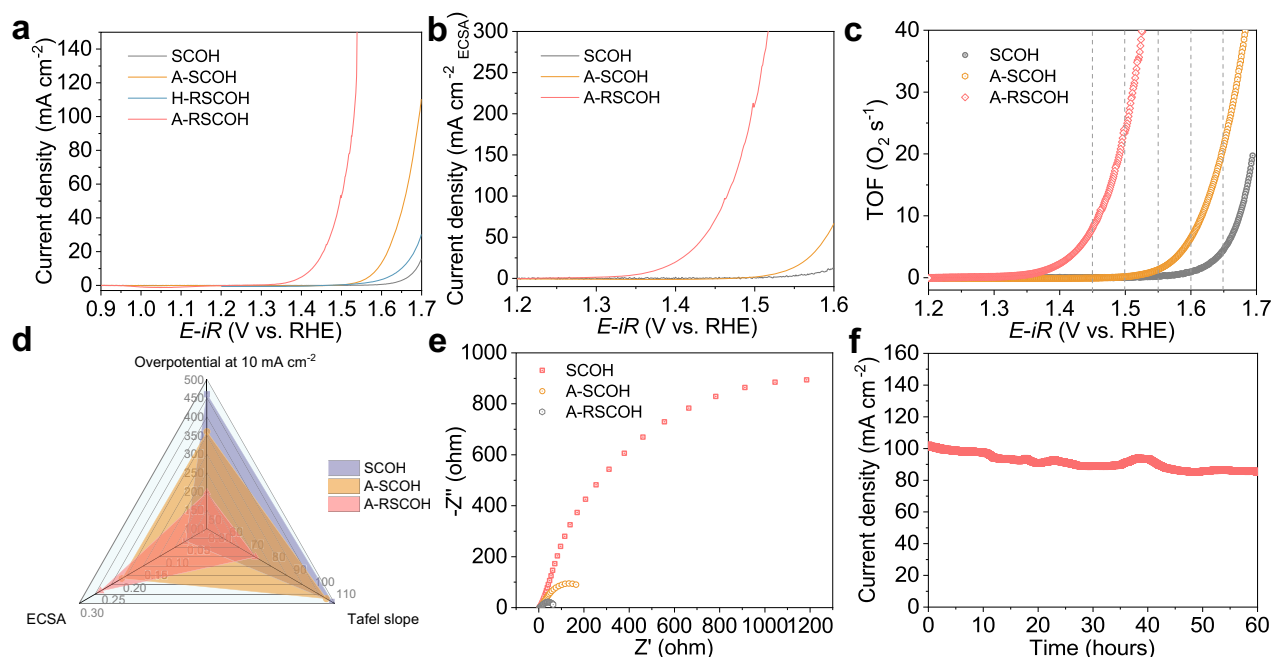


Fig. 3 | Electrocatalytic OER measurements. **a** Polarization curves with 85% iR compensation of electrocatalysts (The scan rate is 5 mV s^{-1} , and the electrode solution resistance is $5.2 \pm 0.1 \Omega$). **b** ECSA normalized current density curves of

SCO, A-SCO, and A-RSCO. **c** TOF values, **d** Comparisons of overpotential, Tafel slope and ECSA, and **e** EIS of the SCO, A-SCO, and A-RSCO. **f** Chronoamperometry stability of A-RSCO at 1.52 V vs. RHE.

potential up to 1.4 V and above. Combining with other characterizations and previous work^{38–41}, the final peaks are ascribed to the vibrational modes of disordered the CoO_2 phase. In addition, a similar variation process occurred for A-SCO under higher applied potentials. The Raman spectra were acquired after the OER stopped for 30 min to keep the electrocatalysts stable. The Raman spectra after the OER are distinct from the spectra before the OER and is similar to the Raman spectra collected at 1.7 V , indicating that the reconstruction process is irreversible.

The morphology characterization of A-RSCO after reconstruction in Supplementary Fig. 30 shows that the nanocube states are maintained. The XPS spectra of A-RSCO after the reconstruction process (R-A-RSCO) are shown in Supplementary Fig. 31, the XPS peaks at 780.4 and 796.1 eV of R-A-RSCO are ascribed to Co^{3+} species^{26–28}. In addition, the XPS peak of the M-O bonds for R-A-RSCO becomes stronger than that for A-RSCO. The above analysis traces the reconstruction process of electrocatalysts under applied potential, and the A-RSCO completes the irreversible reconstruction process to generate high valence metal oxides as active species of the OER under a lower driving potential.

On the basis of a series of characterizations, high valence state metal oxides were identified as active species of the OER. Thus, the calculation models of active species for A-SCO and A-RSCO were selected on the basis of the in situ experimental results and previous work^{42,43}. The calculated magnetic moments of the sites in the active species of A-SCO and A-RSCO are shown in Supplementary Fig. 32, and sites in the active species of A-RSCO exhibits a larger magnetic moment, indicating higher spin density of the sites in the active species of A-RSCO.

Electrocatalytic performance

A typical three-electrode system was utilized to measure the OER performance of all the as-prepared samples in 1 M KOH aqueous solution. The electrocatalysts were preprocessed by 50 cycles of CV under the applied potential of 0.8 – 1.6 V vs. RHE. The optimal A-RSCO only needs the overpotential of 193 mV to achieve

10 mA cm^{-2} , demonstrating superior OER performance compared with that of SCO and A-SCO (Fig. 3a). It is optimized by regulating various synthesis conditions (calcination temperature, atmosphere, time and doping amount of Ru and ion exchange time), and the corresponding linear sweep voltammetry (LSV) curves are shown in Supplementary Fig. 33. Accordingly, the Tafel slope of A-RSCO is the lowest compared with those of SCO and A-SCO, indicating that A-RSCO possesses the most efficient OER kinetic performance (Supplementary Fig. 34 and Fig. 3d).

Moreover, the electrochemically active surface area (ECSA) was evaluated through the electrochemical double-layer capacitance (C_{dl}) method (Supplementary Fig. 35). A-RSCO has a C_{dl} of 0.01 mF cm^{-2} , which is larger than that of SCO (0.002 mF cm^{-2}) and A-SCO (0.008 mF cm^{-2}). Then, the ECSA of all samples was calculated and the OER current density was normalized to ECSA (Fig. 3b). The anodic current density of A-RSCO is still the highest, reflecting outstanding intrinsic activity. The TOF values were also calculated to further explore the intrinsic performance (Supplementary Fig. 36 and Note 4). Compared with other contrast electrocatalysts, the A-RSCO shows much larger TOF values (Fig. 3c). The electroconductibility and kinetics of the charge transfer of electrocatalysts play a key role during the OER, which is measured by electrochemical impedance spectroscopy (EIS). As shown in Fig. 3e, the smallest charge transfer resistance of A-RSCO is obtained from the Nyquist plots, indicating the notable electroconductibility and charge transfer kinetics of A-RSCO. Moreover, the A-RSCO also has decent stability, and no distinct decrease in the anodic current density is observed in Fig. 3f and Supplementary Fig. 37. From the TEM images, the A-RSCO manifests well-retained morphology after long-term chronoamperometry measurements (Supplementary Fig. 38). And the average valence state of metal elements increases slightly (Supplementary Fig. 39). As a consequence, the A-RSCO maintained stable during OER.

Evolution of charge and intermediates

The electrocatalytic OER involves several fundamental processes, leading to difficulties in understanding the complex electrochemical

mechanisms. Thus, kinetic analyses were executed to explore the OER and reconstruction process. As we know, the oxidation of methanol (MeOH) is driven by electrophilic oxygen species, which are relevant to the reaction kinetics during the OER^{44,45}. MeOH molecular probe experiments (MOR) can be conducted to detect the intermediates during the OER. Compared with A-SCOH and SCOH, the A-RSCOH possesses a higher MOR current at low potentials (0.9–1.3 V), indicating stronger OH* adsorption (Fig. 4a and Supplementary Fig. 40). Especially, the strong OH* adsorption could promote the phase transformation⁴⁶, granting a faster reconstruction process of A-RSCOH, which is in agreement with the results of in situ Raman spectroscopy and operando UV-Vis spectroscopy. Moreover, the larger current difference between the MOR and OER reflects that the electrophilic oxygen intermediate is consumed rapidly⁴⁷, in alignment with its active reactivity.

The applied potential could regulate the charge accumulation of catalysts to affect the rupture and formation of chemical bonds during the electrochemical reaction. Based on the premise, pulse voltammetry (PV) was performed to investigate the dynamic evolution of electrocatalysts and intermediates during the OER (Supplementary Note 5)^{48,49}. As shown in Fig. 4b and Supplementary Fig. 41, the curves

of the current response to the impulse voltage can be divided into steady and transient states⁵⁰, corresponding to the evolutions of intermediates and dynamic balancing states. The decay current profile at the anodic and cathodic potentials can be fitted by the Dupont and Donne model⁵⁰, which includes the current profiles of the double-layer capacitor and the diffusion-limited process. Nevertheless, the main mode of charge storage for A-RSCOH is the double-layer capacitance type (C_{dl} -type) according to the fitting results⁵¹. The double-layer capacitance (C_{dl}) and charge could be acquired through fitting the anodic and cathodic current pulse curves. Both the anodic C_{dl} and C_{dl} -type charges for A-RSCOH are higher than the cathodic process at low potential (1.00–1.35 V) (Fig. 4c, d), indicating that the active oxidized species generated through the reconstruction can survive after the revocation of the applied anodic potential. It can be inferred that the reconstruction process is not completely reversible. The tendency to decrease the C_{dl} -type charge is subsequently observed at higher potentials, due to the appearance of bulk redox (C_{diff} -type) related to the OER process, promoting the loss of C_{dl} -type capacitance (Supplementary Fig. 42). In addition, the three sections of total charge in A-RSCOH represent the process of $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$, $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$ and the OER, and the required potential ranges are consistent with the CV curves

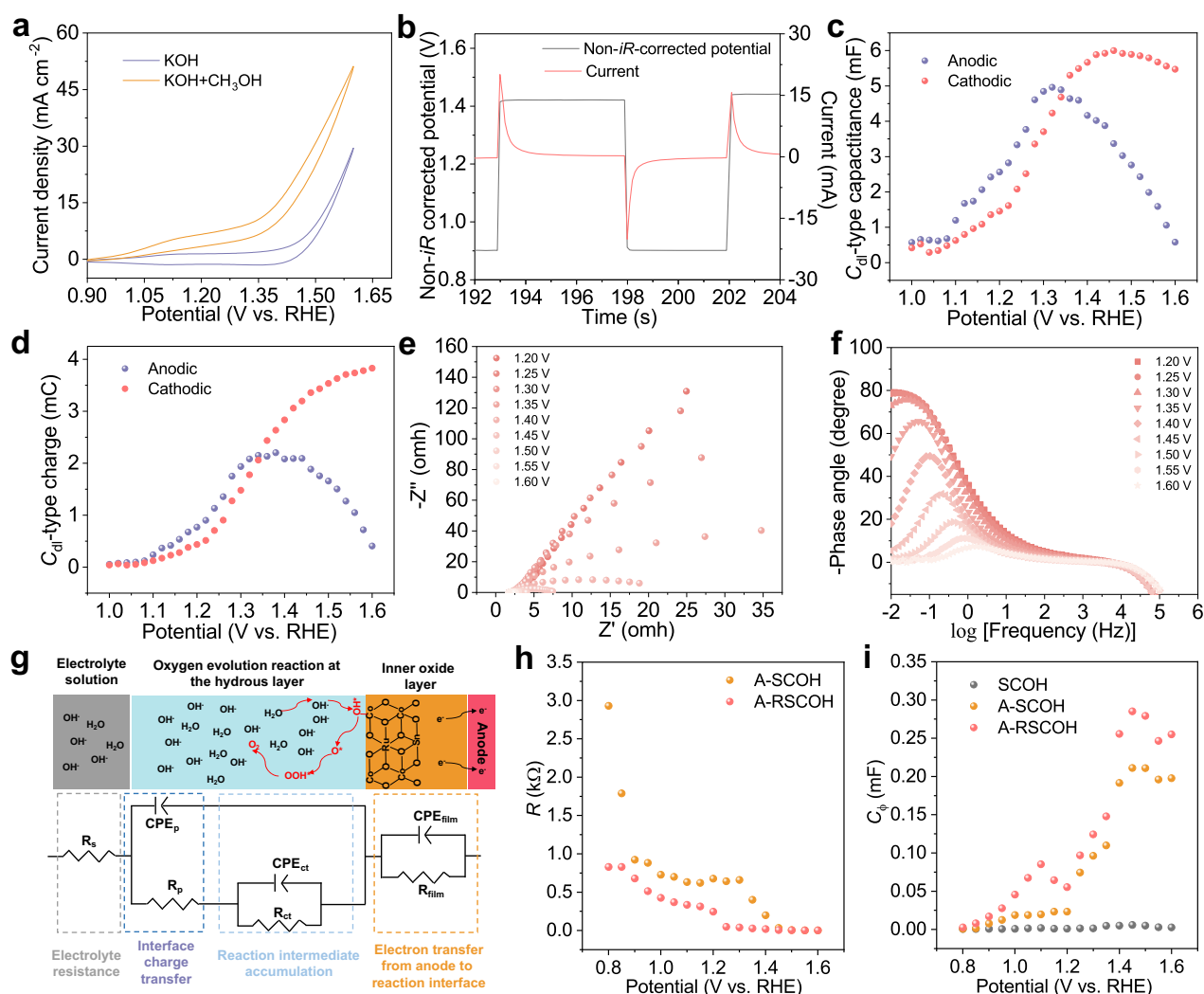


Fig. 4 | Evolution of charge and intermediates. **a** CV curve of A-RSCOH in 1 M KOH with and without 1 M methanol (without *iR* compensation). **b** Anodic/cathodic potential and relevant current density of A-RSCOH extracted from the local part of PV measurements. **c** C_{dl} -type capacitance and **d** charge of A-RSCOH vs. pulse

potential without *iR* corrected. **e** Nyquist and **f** Bode plots of A-RSCOH at different potentials. **g** Equivalent circuit model and illustration of correlations among intermediates, reaction interfaces, and charge transfer. **h**, **i** R_{total} (**h**) and C_{ϕ} (**i**) of A-RSCOH vs. potential.

and in-situ electrochemical spectra (Supplementary Figs. 23–29 and Supplementary Fig. 41). When the applied potential up to 1.45 V vs. RHE, the anodic C_{dl} decreases at a faster rate compared to the cathodic C_{dl} , and the distinction between anodic and cathodic C_{dl} -type charge is linearly dependent on the log (OER current) during the synchronized transient time (Supplementary Fig. 43). These results indicate extremely fast OER kinetics with a depressed charge lifetime of A-RSCOH, which is attributed to the effect of a synchronized source and sink for charge (redox between applied potential and OER elementary steps and the OER).

In situ EIS measurements were conducted to further probe the kinetics during the reconstruction and OER processes (Supplementary Note 6). The Nyquist plots are shown in Fig. 4e and Supplementary Figs. 44–46, revealing the impedance of the whole electrocatalytic system. It includes information on the electrolyte resistance (R_s), intermediate adsorption resistance (R_{ct}), and pseudocapacitance (CPF_{ct}), reflecting the mass transfer, adsorption strength, and coverage of intermediates, respectively^{52–55}. This kinetic information is obtained by fitting Nyquist plots for a suitable equivalent circuit (Fig. 4g). Moreover, the R_{total} values (defined as the total transfer resistance) reflect the R_{ct} values, because of the similar R_s values of each test system. The R_{total} of A-RSCOH is the smallest among all the samples during the entire potential range, indicating that the fastest charge-transfer kinetics occur during the entire reaction process (Fig. 4h and Supplementary Fig. 47). In the range of low potential (0.8–1.3 V), extremely small R_{total} values of A-RSCOH manifest the fastest kinetics of OH^* on the surface to launch a reconstruction process. The fastest decay rate of R_{total} for A-RSCOH indicates that a lower driving force can produce OER active species to initiate a fast kinetics OER process. Moreover, A-RSCOH possesses the largest CPF_{ct} among all the samples, manifesting the fastest accumulation kinetics of OH^* , which is beneficial to the overall electrocatalytic process (Fig. 4i). The Bode phase plots in Fig. 4f and Supplementary Figs. 44–46, can be divided into the high-frequency and low-frequency regions, representing charge conduction during the reconstruction of electrocatalysts and electron transfer at the interface (OER process), respectively⁵⁴. It is reasonable that only the phase angle at high frequency moves before the OER potential. Compared with A-SCOH and SCOH, the phase angle of A-RSCOH at high frequency moves violently under lower potential, indicating faster electron transfer kinetics during the reconstruction process. For SCOH, the shift and reduce in the phase angle at the high-frequency end at a higher potential manifests a tough reconstruction process. The movement of phase angles at low frequency emerges at 1.35 V for A-RSCOH, and the phase angle decreases rapidly. However, the SCOH and A-SCOH do not shift and reduce the phase angle at low frequencies until the applied potential reaches 1.45 V. This phenomenon reflects that the OER for A-RSCOH occurred earlier with faster charge transfer kinetics⁵⁶. Thus, the A-RSCOH possesses admirable adsorption capacity of intermediates and fast charge transfer kinetics for reconstruction and OER process.

Identification of rate-determining step

The CV and DPV curves of A-RSCOH and A-SCOH in different concentrations of KOH solutions are shown in Fig. 5a–c and Supplementary Figs. 48–50, which embody the proton-electron transfer process of active sites⁵⁷. Then Pourbaix diagrams are acquired and fitted through the Nernst equation (Supplementary Note 7). The potentials of Co^{3+}/Co^{4+} redox reactions vary by 0.085 and 0.067 V per unit of pH for A-RSCOH and A-SCOH, respectively (Fig. 5b and Supplementary Fig. 49). The slope of 0.085 V pH^{-1} reflects the super-Nernstian behavior^{58,59} of A-RSCOH, indicating a decoupled proton-electron transfer process (PT/ET) (Fig. 5h). The super-Nernstian behavior of A-RSCOH during Co^{3+}/Co^{4+} indicates the generation of active species with superoxide ligands⁶⁰. However, A-SCOH shows a thermodynamic Nernstian shift, resulting in a concerted proton and electron transfer

process without charged intermediates (Supplementary Fig. 49a). The potential shifts with pH at an OER current density of 2 $mA\ cm^{-2}$ are shown in Fig. 5c, the slopes of A-RSCOH derived by linear fitting close to 110 V pH^{-1} , indicating the pH-dependent OER activities of A-RSCOH⁶⁰. LSV curves were collected in 1 M NaOH and 1 M NaOD to obtain deuterium kinetic isotope effects (KIE), reflecting the kinetic properties of proton transfer during OER (Fig. 5d, Supplementary Fig. 51 and Note 8)^{61,62}. The current density observed in 1 M NaOD is lower than that of 1 M NaOH for all samples. The $KIE_{H/D}$ values are calculated through the equation in Supplementary Note 8. The $KIE_{H/D}$ values of both SCOH and A-SCOH are greater than 1.5 with a primary KIE effect, indicating that the rate-determining step (RDS) is a proton transfer process. The lower $KIE_{H/D}$ values of A-SCOH manifest faster kinetic of OER. The $KIE_{H/D}$ value of A-RSCOH (<1.5) is lower than that of SCOH and A-SCOH, demonstrating secondary KIE effects (Fig. 5d). Therefore, the experimental results reveal that the cleavage of O-H bonds is not included in RDS for A-RSCOH⁶¹.

The reaction order reflects the dependence of the OER kinetics on the proton activity. To determine the proton reaction order, the LSV curves of the samples were collected at electrolytes with different pH. As shown in Supplementary Fig. 52 and Fig. 5e, the OER performance of A-RSCOH improves with the increase in pH. However, SCOH and A-SCOH exhibit similar OER performance at various pH. Then the proton reaction orders ($\rho = \partial(\log j)/\partial(pH)$) are generated through linear fitting a function of log (OER current) with pH. The reaction order of A-RSCOH, A-SCOH, and SCOH is 0.608, 0.069, and 0.031, respectively, reflecting the pH-dependent OER performance of A-RSCOH (Fig. 5f). A concerted proton-coupled electron transfer (CPET) has the comparable ability of electron transfer and proton-coupled, which usually doesn't depend on the pH of the electrolyte. But proton concentration could reflect OER activity, when the proton-coupled and electron transfer take place in succession (DPET process)⁶². Obviously, the reaction mechanism of A-RSCOH is the DPET process, while the OER process of A-SCOH and SCOH is CPET. It can be easily concluded that charged reaction intermediates existed in the DPET process. The tetramethylammonium cation (TMA^+) could trap negatively charged intermediates⁶³. Therefore, the OER activities of samples in 1 M KOH and TMAOH are compared. As shown in Fig. 5g, the OER performance of A-RSCOH in TMAOH descends distinctly compared with in KOH, whereas the similar OER performances of A-SCOH and SCOH are manifested in different electrolytes (Supplementary Fig. 53). This suggests that intermediates with negative charge emerged during OER for A-RSCOH. Combined with other results of kinetic tests, neither OH^* adsorption nor O-H bond cleavage is the RDS. Thus, the RDS is the decoupled electron transfer (ET) procedure in the DPET step.

OER mechanistic insights

On the basis of the above findings, the calculation model of the active species for A-SCOH and A-RSCOH was constructed (Supplementary Fig. 54)^{42,43}. According to molecular orbital theory, the M-O bond could split into bonding bands ((M-O), oxygen character) and antibonding bands ((M-O)*, metal character), which are driven by the charge transfer energy. Furthermore, d-d Coulomb interaction (U) induces (M-O)* bands to split into empty upper-Hubbard bands (UHB) and filled lower-Hubbard bands (LHB)⁶⁴. The electronic structure information can be reflected by DOS. As shown in Fig. 6ac, the band alignment of active species for A-SCOH corresponds to the ionic character of the metal-oxygen (M-O) bond, which is called the Mott-Hubbard insulator⁶⁵. Under these circumstances, metal cations are thermodynamically favorable to transfer electrons to reaction intermediates because of the positive energy difference between metal d and oxygen p band centers. The DOS of active species for A-RSCOH shows increased hybridization of the metal d and oxygen p band, indicating the improvement of covalency for the M-O bond. In

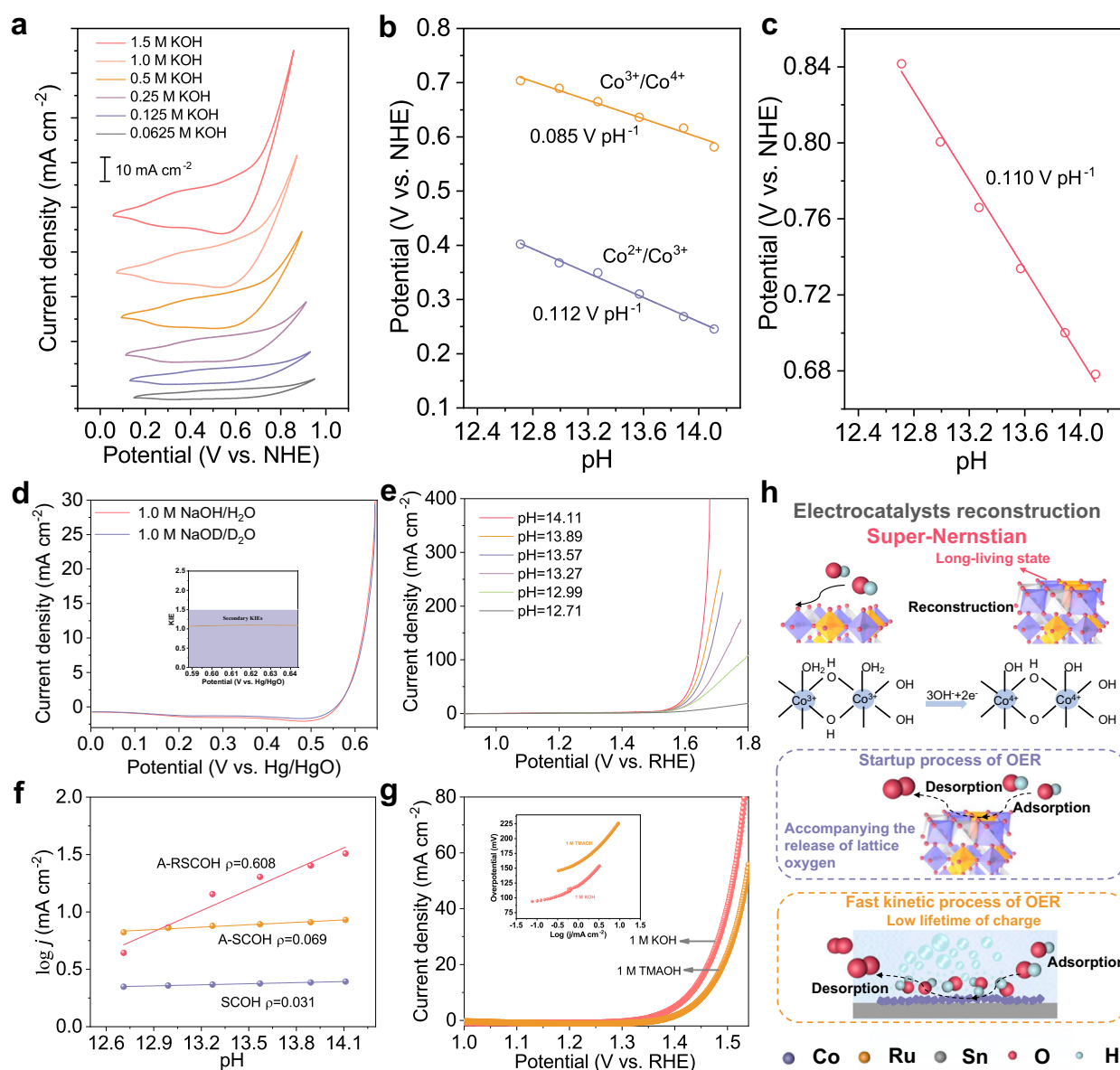


Fig. 5 | Identification of rate-determining step. **a** CV curves of A-RSCOH in electrolytes with different pH and **(b)** relevant Pourbaix diagram (without iR compensation). **c** Fitting plot of applied potential at 2 mA cm^{-2} vs. pH of the electrolyte. **d** Polarization curves of A-RSCOH in $1 \text{ M NaOH/H}_2\text{O}$ and $1 \text{ M NaOD/D}_2\text{O}$ and

corresponding KIE values vs. potential are shown in the inset. **e** LSV curves of A-RSCOH in electrolytes with different pH. **f** Current densities of electrocatalysts at 1.6 V vs. RHE in electrolytes with different pH. **g** LSV curves of A-RSCOH in 1 M KOH and 1 M TMAOH . **h** Schematic diagram of proton/electron transfer process.

addition, after Ru doping, the DOS of Co and O around the Fermi level (E_F) improves distinctly. As well known, the DOS around E_F represents the total charge carrier density, which could reflect the ability of electron transfer for the electrocatalyst. Thus, the Ru stimulates intramolecular electron transfer to form a negative charge transfer insulator⁶⁶, improving the ability of electron transfer for Co and O sites. Moreover, high energy non-bonding states oxygen (O_{NB} , oxygen holes) emerges in active species for A-RSCOH, which is equipped with radical character and activates lattice oxygen (Fig. 6a). The differential charge density and electron localization function present the apparent electronic structure information in an intuitive perspective (Fig. 6b), and reveal that more drastic electron delocalization occurs in active species for A-RSCOH, demonstrating increased covalency of Co-O bonds.

Afterward, SCOH, A-SCOH, and A-RSCOH were labeled with ^{18}O isotopes to evaluate the flexibility of the lattice oxygen (Supplementary Note 9 and Supplementary Fig. 58). The labeled electrocatalysts

conducted CV tests in 0.1 M KOH with H_2^{16}O within the range of 1.0 V - 1.6 V , and the reaction products were detected by differential electrochemical mass spectrometry (DEMS). Negligible $^{18}\text{O}^{16}\text{O}$ and $^{18}\text{O}^{18}\text{O}$ signals are detected from the products of SCOH and A-SCOH (Supplementary Fig. 55). Distinctively, the DEMS signals of $^{18}\text{O}^{16}\text{O}$ for A-RSCOH are evident, but scarcely any signals of $^{18}\text{O}^{18}\text{O}$ are observed. Therefore, the lattice oxygen of A-RSCOH participated in the OER, and only half of the O in the products was derived from H_2O . The curves of the normalized $m/z=34$ and 36 signals varying with the applied potential of the CV tests are shown in Fig. 6d and Supplementary Fig. 56, where the normalized $m/z=34$ of A-RSCOH increases when the potential increases to 1.32 V , indicating the consistency of DEMS signals and the OER current density. No variations of normalized signals are noticed for SCOH and A-SCOH, which is consistent with the above analysis. The intensity of the $^{18}\text{O}^{16}\text{O}$ signals produced by A-RSCOH gradually decreases as the number of cycles increases, which is

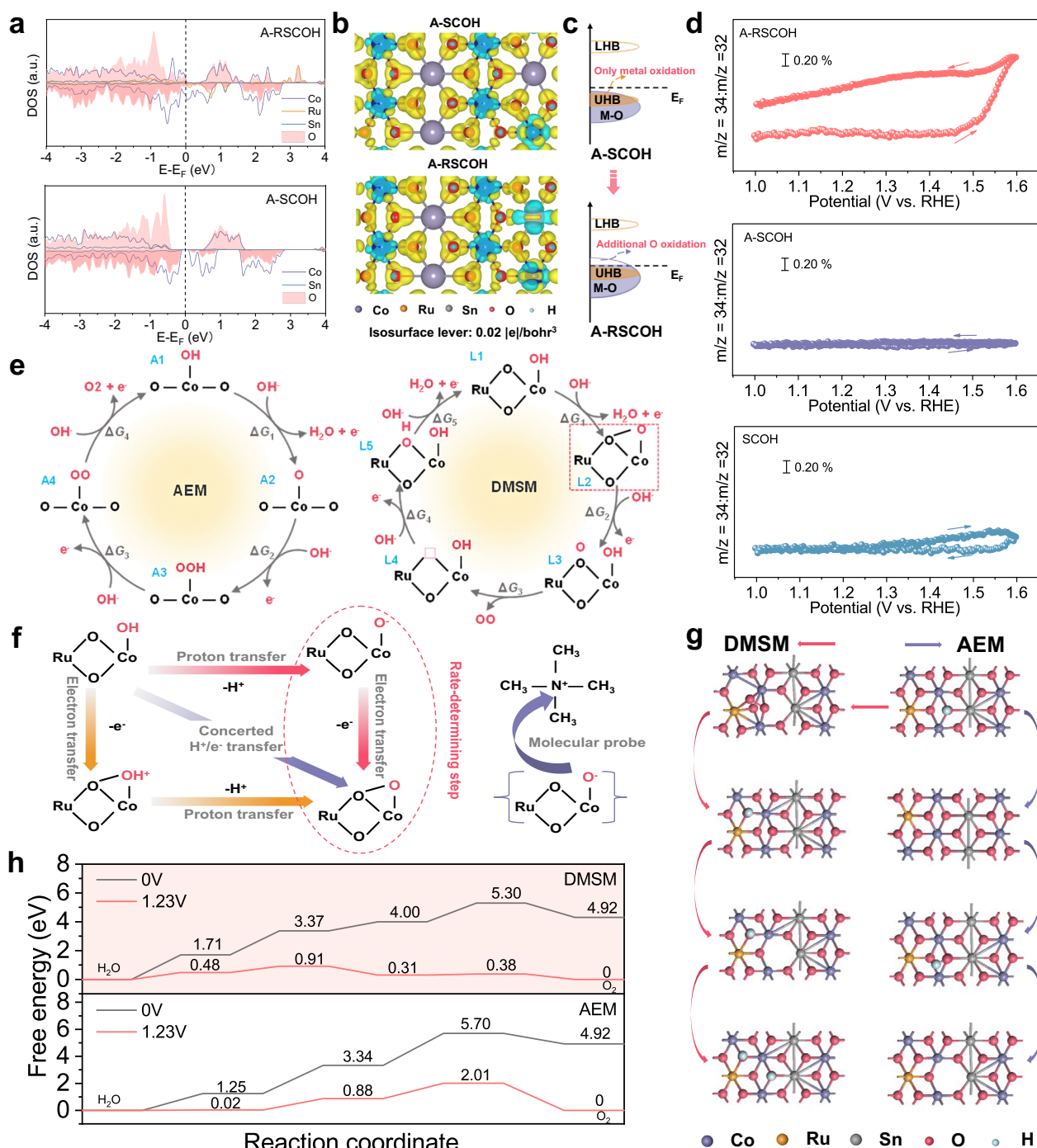


Fig. 6 | Correlation between the electronic structure of catalysts and OER mechanism. **a** DOS of Co, O, Ru, and Sn orbitals in active species of A-RSCOH and A-SCOH. **b** Difference in charge density of active species of A-RSCOH and A-SCOH (the cyan colors represent charge depletion, and the yellow represents charge accumulation). **c** Energy bands structure of active species of A-RSCOH and A-SCOH

under Mott-Hubbard splitting. **d** Variations of DEMS signals of $^{34}\text{O}_2$ for various electrocatalysts along with CV cycles. **e** Schematic of OER mechanisms. **f** Illustration of sequential and concerted proton-coupled electron transfer reactions for rate-determining step. **g** Adsorption models evolution process of AEM and DMSM. **h** Gibbs free energies of active species of A-RSCOH for different mechanisms.

attributed to the consumption of ^{18}O labeled lattice oxygen. In conclusion, the lattice oxygen is engaged in the OER process.

On the basis of DEMS, specially, the lattice oxygen was engaged in OER for A-RSCOH. The reaction pathways with and without the participation of lattice oxygen and the free energy barriers (ΔG) were calculated to discuss the OER mechanism (Fig. 6g). As shown in Supplementary Fig. S7, A-SCOH tends to follow the traditional adsorbate evolution mechanism (AEM) thermodynamically. Firstly, OH^- in

electrolyte chemisorbs on metal sites to launch OER. Then the deprotonation, O-O coupling and desorption take place successively to complete OER, demonstrating an RDS of 0.82 eV. The reaction pathway of negative charge transfer insulator (A-RSCOH) is different from A-SCOH, and the specific procedures are shown in Fig. 6e. The OH^- also adsorbs on metal Co sites firstly, and occurs deprotonation immediately. Distinctively, the Co-O-Ru bond is broken, and the lattice oxygen is coupled with the absorbed $^*\text{O}$ to proceed with the

subsequent OER procedure. Then, the chemical bonds are broken, and the acquired $\ast\text{OO}$ from the previous step transforms into an O_2 molecule. Finally, the OH^- in the electrolyte is absorbed on the Ru and Co site to replenish the released lattice oxygen for the next OER cycle. The A-RSCoH is confirmed to obey the dual-metal-site mechanism (DMSM)⁶⁶, and the ΔG of RDS is calculated to be 0.48 eV (Fig. 6h).

Considering the limitations of DFT calculations, a more detailed OER procedure should be discussed in combination with experimental analysis (Fig. 5 and Supplementary Figs. 48–53). The pH-dependent measurements reveal the existence of the DPET procedure of A-RSCoH during OER. The TMA^+ chemical probe captures the negative oxygenated species. The secondary KIE effects of A-RSCoH indicate that the cleavage of O–H bonds is not included in RDS for A-RSCoH. Specifically, only the slowest step in the catalytic cycle is experimentally accessible by steady-state measurements. Thus, the above-observed phenomenon is closely related to RDS. Combined with the results of kinetic tests, we concluded that the RDS is the decoupled electron transfer (ET) procedure for the formation of a metal-oxygen bridge bond (Fig. 6f).

Discussion

In summary, we reported a ruthenium-cobalt-tin oxide (A-RSCoH) as an efficient OER electrocatalyst. The doping of Ru induces the quantum spin interaction of Ru and Co, optimizing the spintronic structure of A-RSCoH, and promoting the favorable charge transfer kinetics and intermediates evolution behavior under applied potential. The reconstruction process produces the long-lived active species with higher spin density sites for the subsequent OER process. The A-RSCoH shows the dependency of proton activity, demonstrating the existence of the DPET step during the OER process. Combined with theoretical calculations, the rate-determining step was identified as an electron transfer procedure of O–O bond formation between $\ast\text{O}$ intermediate and the lattice oxygen in Co–O–Ru. This work not only provides the principle for the rational design of OER electrocatalysts but also constructs the correlation between spintronic structure, surface reconstruction, and OER mechanism.

Methods

Chemicals

Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\geq 99.99\%$), sodium citrate ($\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$, $\geq 99.5\%$), tin(IV) chloride hydrated ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\geq 99\%$), sodium hydroxide (NaOH , $\geq 97\%$), potassium hydroxide (KOH , $\geq 95\%$), ruthenium(III) chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $\geq 99.95\%$) were purchased from Aladdin. Tetramethylammonium hydroxide (TMAOH, $\sim 25\text{ wt}\%$ in H_2O), deuterium oxide (D_2O , $\geq 99.9\text{ atom}\%$ D), and deuterium sodium oxide solution (NaOD in D_2O , $40\text{ wt}\%$) were purchased from Sigma-Aldrich. ^{18}O isotope-labeled H_2^{18}O ($97\text{ atom}\%$ ^{18}O) bought from Wuhan Isotope.

Fabrication of $\text{SnCo}(\text{OH})_6$

The $\text{SnCo}(\text{OH})_6$ (labeled as SCOH) was fabricated through a modified co-precipitation method. 2 mmol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 0.3 M sodium citrate aqueous solution and stirred for 30 min. The solution was cooled down below 273 K before subsequent operation. Then, 10 mL of 0.2 M SnCl_4 aqueous solution was dropped in the cooled solution and stirred for another 30 min. After that, 2 M NaOH solution was added to the above solution drop by drop until the pH value was tuned to 10, and more 30 min stirring was maintained to obtain pink-colored precipitates. The pink-colored precipitates were washed with water and ethanol several times and dried in a vacuum oven at 333 K for 24 hours.

Fabrication of amorphous- $\text{SnCo}(\text{OH})_6$

The prepared $\text{SnCo}(\text{OH})_6$ was further annealed at 573 K in H_2/Ar (5%/95%) atmosphere for 30 min to obtain amorphous- $\text{SnCo}(\text{OH})_6$

(labeled as A-SCoH). Other annealed temperatures (373, 473, and 673 K), atmosphere (air), and time (60, 120 and 180 min) were applied to acquire contrast samples.

Fabrication of amorphous- $\text{RuSnCo}(\text{OH})_6$

The amorphous- $\text{RuSnCo}(\text{OH})_6$ (labeled as A-RSCoH) was synthesized by an ion exchange-pyrolysis procedure. Firstly, 25 mg A-SCoH was dispersed in deionized (DI) water. Moderate $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (0.02, 0.03, 0.04, 0.05 mmol) was added to 10 mL DI water to obtain a homogeneous solution and then dropped into the above suspension under stirring conditions. The ion exchange-pyrolysis sustained for a while (2–8 h) at room temperature, the product was collected after washing by DI water and ethanol and dried at 333 K overnight (generated sample is labeled as H-RSCoH). Finally, the dried precipitate was pyrolyzed at 573 K for 4 h (generated sample labeled as A-RSCoH).

Characterizations

The phases were confirmed by X-ray diffraction spectrum (XRD, Japan Rigaku Rotaflex). The scanning electron microscope (SEM, SU5000), energy-dispersive X-ray spectrum (EDS), transmission electron microscopy (TEM, JEM-F200), and spherical aberration-corrected TEM (JEM ARM200F) were applied to explore the morphology and elementary composition of samples. The electronic structure of electrocatalysts was characterized by X-ray photoelectron spectroscopy (XPS, Thermo Fisher, ESCALAB 250 Xi). Raman and in situ Raman spectra were performed on Renishaw Invia Qontor Raman spectrometer with an excitation wavelength of 532 nm and a 50x objective. The ultraviolet-visible absorption spectra (Shimadzu UV-3600 Plus) were conducted to record operando UV-Vis spectra. The magnetic properties and spin structure were characterized by a physical property measurement system (PPMS, DynaCool). The differential electrochemical mass spectrometry (DEMS) was measured by QAS 100 mass spectrometry (Linglu Instruments, Shanghai). The XAFS spectra were recorded at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility by transmission mode. The measurement details are exhibited in supporting information.

Working electrode preparation

2 mg carbon powder and 2 mg electrocatalysts were dispersed in 400 μL isopropanol with 15 μL Nafion to acquire inks. The glassy carbon electrode (GCE) with a diameter of 3 mm was polished with alpha alumina powder. The carbon fiber papers (the working area is 1 cm^2) were washed with DI water, acetone, and ethanol in sequence. The working electrode was obtained by dropping 15 μL ink on GCE or dropping 215 μL ink on carbon fiber paper.

Electrochemical measurements

The electrochemical characterization were conducted on a CHI 760E by a three-electrode system, which employed prepared electrocatalysts on GCE or carbon fiber papers as work electrode, Pt wire as counter electrode, and Hg/HgO electrode as reference electrode. The chronoamperometry measurement used carbon fiber papers as the working electrode, while other electrochemical tests used GCE as the working electrode. Specifically, Hg/HgO was calibrated by cyclic voltammetry in H_2 -saturated 1 M KOH electrolyte using a purified Pt wire as the working and counter electrode. A cyclic voltammogram (CV) was recorded at a scan rate of 1 mV s^{-1} , with the thermodynamic potential for the hydrogen electrode reactions identified from the point where the current intersected zero. All electrolyte solutions were prepared on demand by dissolving KOH into deionized water and were stirred for 1 h to realize a homogeneous state. All measurements proceeded in 1 M KOH ($\text{pH} = 13.89 \pm 0.1$) at room temperature ($298 \pm 2\text{ K}$), and potentials were unified by the Nernst equation: $E_{\text{RHE}} = E_{\text{Hg}/\text{HgO}} + 0.059\text{ pH} + 0.098$. The effect of solution resistance was considered, and the potentials were corrected by the following equation:

$E_{\text{corr}} = E_{\text{meas}} - iR_s$, where the R_s were generated from the Nyquist plots ($5.2 \pm 0.1 \Omega$ in 1 M KOH). The linear scan voltammetry (LSV) tests were conducted from 0.9 to 1.6 V vs. RHE with a scan rate of 5 mV s^{-1} , and the polarization curves were 85% iR corrected unless specific statements. The overpotential of electrocatalysts was calculated through the equation of $\eta = E_{\text{RHE}} - 1.23 \text{ V}$. Tafel slopes were acquired by fitting to the Tafel equation: $\eta = b \log j + a$, where η , j and b are overpotential (mV), current density (mA cm^{-2}) and Tafel slope, respectively. Electrochemical impedance spectroscopy (EIS) was tested from 100 kHz to 0.1 Hz with 5 mV amplitude. The double-layer capacitance (C_{dl}) was obtained by cyclic voltammetry (CV) with various scan rates under no Faradaic region. The electrochemical active surface area (ECSA) was calculated by the formula of $\text{ECSA} = C_{\text{dl}}/C_s$, where C_s (the value is $40 \mu\text{F}$ in this study) is the specific capacitance of electrocatalysts. All samples were activated by CV before electrochemical measurements. Other measurement details are exhibited in supporting information.

Calculation Setup

The Vienna ab initio simulation package (VASP)^{67–70} was used to perform the density functional theory (DFT) calculations. The exchange-correlation energy⁶⁷ was described by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. The Projector-augmented wave (PAW) technology⁶⁸ was employed to describe the core electrons. The value of cut-off energy for plane wave basis was defined as 550 eV.

The structure convergence criteria and force convergence threshold were set to 10^{-4} eV and $0.01 \text{ eV \AA}^{-1}$, respectively. DFT + U method was used due to the strong d-electron correlation effects^{69,70}, and the U_{eff} for Co and Ru were defined as 3.5 eV and 2.0 eV, respectively.

To construct the amorphous structure of A-SCOH, the MD simulation was performed on the $\text{Co}_4\text{Sn}_4(\text{OH})_{24}$ under the NVT ensemble at 573 K according to the experimental condition. The time step was set as 1 fs and the total simulation time was 5 ps with 5000 steps. As the simulation time increased, the model started to become amorphous. After the MD finished, the geometry optimization was carried out to obtain the stabilized amorphous structure as the A-SCOH. Moreover, a Sn atom in the cluster was replaced by a Ru atom followed by the geometry optimization to acquire the model of A-RSCOH. The initial and final configurations of MD simulation and the optimized structural models are supplied in Supplementary Data 1.

Data availability

The data that support the findings of this study are available in the file of Source Data. Source data are provided in this paper.

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Acknowledgements

This work was supported by the National Key R&D Program of China (2023YFA1507101 and 2022YFA0911900), the National Natural Science Foundation of China (Nos. 22372021 and 22088102), the Fundamental Research Funds for the Central Universities (No. DUT22LAB602) and Special Project for Key Research and Development Program of Xinjiang Autonomous Region (2022B01033).

Author contributions

J.H. supervised the research. J.H. and C.W. conceived the research. C.W., P.Z., D.J., and B.S. carried out the experiments. C.W. collected and analyzed the experimental data. C.D., X.S., and J.G. conducted theoretical calculations. C.D. and C.W. analyzed the results of theoretical calculations. W.L. gave helpful advice to analyze XAFS data. L.S. gave helpful advice on the manuscript preparation. C.W. and J.H. wrote the paper.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41467-024-55688-8>.

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Peer review information *Nature Communications* thanks the anonymous reviewer(s) for their contribution to the peer review of this work. A peer review file is available.

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