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Peer Review File

Bioinspired Sulfo Oxygen Bridges Optimize Interfacial Water Structure for Enhanced Hydrogen Oxidation and Evolution Reactions

Corresponding Author: Professor Jintao Zhang

Parts of this Peer Review File have been redacted as indicated to remove third-party material.

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript focuses on simulating the creation of cobalt and ruthenium atom pairs (Co-SO-Ru) in biology to optimize the interface water for advanced hydrogen electrocatalysis. However, many previous studies have used atomic pairs and interface structures to enhance performance. So, this manuscript lacks novelty, and I will not recommend publication.

As for simulation biology, it is just a gimmick and not the focus of the author's work. Although the author constructed a single atom, only a simple characterization was carried out, and the performance of the entire article is mainly attributed to the atomic pairs and interface structure. The authors' claim of observing single-atom sites on the carbon support is overstated and insufficiently supported by the presented data (lines 112-114). While it is true that signal intensity in HAADF-STEM images correlates with atomic number (Z-contrast), it is crucial to acknowledge that other factors, particularly sample thickness, can significantly influence the observed intensities. The decrease in intensity may be due to the superposition of fewer atoms rather than the presence of a single atom. This fundamental ambiguity significantly undermines the validity of the author's claims regarding the distribution of Co atoms. Therefore, the presented data does not adequately support the claim of observing single-atom sites on the carbon support. Given the limitations mentioned above, the current analysis does not provide conclusive evidence for the presence of isolated atoms.

In addition, the XRD data analysis has shortcomings. The XRD data has significant noise, and efforts can be made to improve its quality. So, the synchrotron radiation XRD (or even synchrotron radiation on the distribution function) of the material can be further performed for analysis.

Reviewer #2

(Remarks to the Author)
In this manuscript, the authors present stereoscopic sulfo-oxygen bonds bridging Co and Ru atomic pairs as highly active sites for advanced hydrogen catalysis. The Cos-SO-Ru structure demonstrates superior catalytic performance in both the hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER), surpassing commercial Ru/C and Pt/C catalysts. The authors convincingly show that the sulfo-oxygen bridges enhance the hydrogen-bond network by repelling cations from the Ru electrode surface, offering a novel approach to modulate interfacial environments at the atomic scale. These findings are significant and provide fresh insights into the development of efficient HOR catalysts. I recommend the manuscript for publication in Nature Communications, pending minor revisions as outlined below:
1. For the formation mechanism of stereoscopic sulfo-oxygen bonds, a more detailed explanation is required to strengthen the understanding of how these bonds are formed.
2. Please include the XPS data for oxygen elements obtained at different temperatures, aimed to clarify how temperature influences the bonding environment.
3. Why Cos-SO-Ru achieves optimal H* adsorption-desorption energy. Further discussion of this point would help clarify the underlying factors contributing to the enhanced catalytic activity.

4. It would be interesting to explore whether a Co(Ru)-organic precursor with abundant hydrophilic counter anions (SO_4^{2-}) could exhibit improved HER catalytic performance, potentially due to stronger hydrogen-bond networks. If possible, this hypothesis could be tested or discussed, as it would provide key evidence of the role of hydrophilic groups in facilitating hydrogen catalysis.
5. Minor revisions: Correct the positioning of Figure 5 and amend the wording in line 323, changing "sorption" to "adsorption." Also, address any other minor errors throughout the manuscript.

Reviewer #3

(Remarks to the Author)
This work is interesting and valuable, but it must address the following comments before it can be accepted.

1. Fig.3a, the S2p fitting has some problem, please redo it and explain.
2. for the long-term stability test by CP at 50 mV. what do you mean 50 mV? also the Cos-SO-Ru decreases 12% in 10 h, which is poor catalyst. moreover, the Pt/C is worse, which is also very weird.
3. The long-term stability at small current density for 10 h is meaningless to me. We usually run 1000 h for high current density.
4. The catalyst for HOR in a real fuel cell test is recommended
5. Why alkaline and seawater conditions were used? I did not see any comparison.
6. It seems the HER current start before 0 V vs. RHE for some catalysts. please explain. Also, a high current density comparison is required.

Reviewer #4

(Remarks to the Author)
Yang et al. have investigated how sulfur oxygen bridges optimize the role of interfacial water in alkaline hydrogen electrocatalysis in alkaline electrolytes. The efforts to carry out this work are commendable for the fast-growing field of alkaline hydrogen electrocatalysis. However, after addressing my comments, the work could be published in the prestigious Nature Communications.

1. As the focus of the paper is on alkaline HOR, The tile should read "Sulfo-oxygen bridges optimize interfacial water for alkaline hydrogen oxidation/evolution reactions".

2. Page 3, Introduction Line 46-47, "Efficient conversion between hydrogen evolution and oxidation reactions (HER and HOR) is of importance in achieving a sustainable hydrogen economy...." This is unclear. Proofread the manuscript throughout to enhance clarity.

3. Ruthenium is a noble metal, could authors use non-precious metals such as Ni instead of Ru? Is this idea still valid? The control experiment with Ni should be included.

4. The Cos-SO-Ru system is characterized in depth, especially the insitu ATR-FTIR, XANES, and DFT investigation, and shows a strong bonding with water which is nice. How can we prove its direct effects on the HOR or HER?

5. The intrinsic HOR activity (Figure 4c) should be normalized with the electrochemical active surface area (ECSA) which takes care of the loading and particle size effect. The ECSA determination should be done using Cu-stripping charge for the investigated system to see the real improvement in the performance for precise estimation (Neergat, M., V. Gunasekar, and R. K. Singh. "Oxygen Reduction Reaction and Peroxide Generation on Ir, Rh, and their Selenides–A Comparison with Pt and RuSe." Journal of the Electrochemical Society 158.9 (2011): B1060.).

6. The HOR mass-activity comparison with the literature should be compared to the synthesized materials in this investigation.

7. On page 9, lines 182-183, "According to the Koutecky-Levich equation, the slope for HOR at Cos-
183 SO-Ru electrode determined is 4.51 cm2 mA-1s-1, similar to the theoretical value...." There is no support for the theoretical value. The author should also include the electron transfer during the HOR.

8. The author should compare the HOR exchange current density with the literature results in Figure 4. For instance, how does it compare with the Ru-based catalyst reported in the literature?
Chen, Luyun, et al. "Confining Flat Ru Islands into TiO2 Lattice with the Coexisting Ru–O–Ti and Ru–Ti Bonds for Ultra-Stable Hydrogen Evolution at Amperometric Current Density and Hydrogen Oxidation at High Potential." Advanced Science: 2410881;
Zhu, Y., Klingenhof, M., Gao, C. et al. Facilitating alkaline hydrogen evolution reaction on the hetero-interfaced Ru/RuO2 through Pt single atoms doping. Nat Commun 15, 1447 (2024) https://doi.org/10.1038/s41467-024-45654-9;
Zhou, Y., Xie, Z., Jiang, J. et al. Lattice-confined Ru clusters with high CO tolerance and activity for the hydrogen oxidation reaction. Nat Catal 3, 454–462 (2020). https://doi.org/10.1038/s41929-020-0446-9

9. The CO-poisoning tests for HOR should highlight the robustness of the catalyst with CO tolerance in the hydrogen-fed anode for fuel cell applications.

10. The HOR polarization presented in Figure 4a can be extended to a higher potential of ~0.8 V vs. RHE.

11. The focus of the paper is on alkaline HOR. Why anion-exchange membrane fuel cell test was not performed? The authors should justify their take on this. A few sentences should be included on the AEMFC in the introduction to improve the broadness of the article.

12. In Figure 4i, the HER performance of the Pt looks very low. Authors are advised to check the literature data to justify this.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
Although the author has explained the novelty issue and improved the data quality, there are still some serious problems, as follows.
1. The synchrotron radiation absorption spectrum is essential data for verifying the structure. Although the data shows that there is no Co-Co bond length in the sample, this is in line with the author's expectations. However, we found serious issues with the data of the standard sample Co-Foil. As a conventional sample, the Co-Co bond length of Co-Foil is much smaller than the normal value (around 2.5 Å). This is very strange, so we reasonably doubt the authenticity of the author's data.
2. Regarding our question that the data provided in the HAADF-STEM graph does not fully support the existence of single atoms on carbon carriers, the response that the author's intention never claimed the existence of single atom positions on carbon substrates is not valid. Because some of the author's data, such as synchrotron radiation absorption spectra, clearly show the absence of Co-Co bond lengths in the sample, and the author's response also states that "the author believes that atomic dispersed Co sites cannot be directly observed in HAADF-STEM images due to the weaker signal intensity of Co species compared to Ru species". All of these indicate that the author himself agrees with the viewpoint of Co atom dispersion.
The author believes that "the inability to observe atomically dispersed Co sites in HAADF-STEM images directly is due to the weaker signal intensity of Co species compared to Ru species" cannot be used as a reason for the insufficient quality of HAADF-STEM data, as in the reference "Single-atom Mo tail high-entropy all ultrathin nanosheets with intrinsic tensile strain enhancement electrocatalysis, Nature Communications, 2024." Mo species have weaker signal intensity than Pt species but can still be well displayed. Therefore, the author is responsible for improving the quality of HAADF-STEM to verify this.
In addition, we have found that the resolution of HAADF-STEM is not high enough. Please improve the quality.
Please provide the high-resolution mapping of aberration-corrected electron microscopy, which will more clearly display the structural information of the sample, which is very important.
3. The wavelet transform of the synchrotron radiation absorption spectrum can clearly show the coordination of metals. Please supplement this data.
4. Please improve the data quality of Figure 2g.
5. Please enhance the aesthetic level of Figure 5f.

Reviewer #3

(Remarks to the Author)
The authors have addressed most of my concerns, and it can be accepted now.

Reviewer #4

(Remarks to the Author)
The authors answered satisfactorily the comments raised by doing the additional experiments. Therefore, I accept the manuscript after answering minor comments:

1. In the introduction Page 3, lines 48-51 "The sustainable hydrogen cycle has been considered as a viable strategy to reduce the consume of fossil fuels1,2. Compared with proton exchange membrane fuel cells, hydroxide exchange membrane fuel cell (AEMFC) and water electrolysis (AEMWE) technologies are attractive for renewable hydrogen economy3-5, which allow for exploring cost-effective nonplatinum catalysts for efficient hydrogen evolution and oxidation reactions (HER and HOR)6-8"
Only reference 5 deals with AEMFC, please include the AEMWE and AEMWE papers and cite close to AEMFC or AEMWE for clarity. For instance "AEMFC (Refs..xx) and AEMWE (Refs. yy...) and follow the same throughout the manuscript.

2. Figure 4c, the jo values must be normalized with ESCA. Now it is not clear how it was normalized. Follow the Jo values shown in SI Figure 29.

3. In Supplementary Table 6, it is unclear how jo was compared, it must be compared to mA cm-2ECSA. Authors are advised to revise accordingly. The Supplementary Tables 5 and 6 can be combined into one.

4. On Page 9, The quoted text needs to be revised "The Cos-SO-Ru shows a higher j0 (3.51 mA cm-2) (Fig. 4c) and normalized mass activity (jk,m) (3.44 A mgmetal-1) than those of Cos-Ru and other state-of-the-art electrocatalysts (Supplementary Table 5, 6)"
Jo should be compared to ECSA which is not the case here. The English must be polished throughout the manuscript e.g., "Supplementary Table 5, 6)" should be written as "(Supplementary Tables 5, 6)".

5. The line numbers and the Figure numbers in the rebuttal is different from the article. Unify them for clarity.

6. Why CoNi-SO/C is not active towards HOR? The author is advised to give more insight on this to solidify the impact.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
Regarding the issues with the article "Sulfo oxygen bridges optimize interfacial water for hydrogen electrocatalysis", although the author has provided some explanations, we still feel that there are some unreasonable aspects. We hope that the author can further explain and correct the following issues.
1.Regarding the bond length of the absorption spectrum, I previously pointed out that there were issues with the data processing of the bond length of the Co-Coil standard sample (Figure 3). Although the author explained that the reason for the bond length in the figure being 2.18 Å instead of the actual 2.47 Å was due to the lack of "Phase Correction". Firstly, performing "Phase Correction" is a necessary operation for absorption spectrum processing. Most literature will perform "Phase Correction" processing to obtain the actual bond length, as this is the real data we need. In this response, the author found that the actual bond length of Co-Coil was 2.47 Å after reprocessing it with "Phase Correction". So, what about the other data? Did they also be plotted without undergoing "Phase Correction" processing? For readers, this is a behavior that can easily cause misunderstandings and may even involve academic misconduct, so it is very necessary for us to conduct a detailed examination of this data. Please provide the results of each absorption spectrum with and without "Phase Correction". And please note in the caption of the main text whether the data has undergone "Phase Correction" to avoid any misunderstandings.
2.From the latest HAADF-STEM and wavelet transform of absorption spectra provided by the author (Supplementary Figure 22), the phenomenon of single atoms is still very obvious. However, due to the author's non-standard "Phase Correction", I am not sure if there is also a problem with the processing of wavelet transform. This requires the author to provide the results of whether each data of the absorption spectrum extension edge has and does not have "Phase Correction" before I can infer whether there is a problem with the wavelet transform.
3.Based on the absorption spectrum data reprocessed by the author, the actual bond length of Co-Coil has shifted to the right. It can be reasonably inferred that other data may also shift to the right after undergoing "Phase Correction"? If that's the case, from the perspective of absorption spectrum, the material is not entirely monatomic. The author cannot attempt to avoid this point by deliberately releasing data that has not undergone "phase correction" to confuse the reader's perspective and attempt to verify single atoms. The author should honestly accept this, acknowledge the impurity of the sample, and focus the article on the characterization of HAADF-STEM and the correlation between structural properties. Or can the author provide other reasonable explanations for this?
4.Additionally, please continue to enhance the images and article, as Figure 5f has hardly improved.

Reviewer #4

(Remarks to the Author)
The authors have answered my comments in full. Therefore, I recommend the publication of the manuscript.

Version 3:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
Seggest to accept it.

Point-to-Point Responses to Reviewers' Comments

We appreciate the reviewers for their helpful and insightful comments, which have greatly helped us to improve the quality of our work. The manuscript has been carefully revised accordingly and the detailed responses and quotations from the revised manuscript are listed below. All the revised parts are highlighted in blue in the manuscript.

Reviewer #1:

To provide thorough and clear responses to these general comments, we have divided them into two parts and addressed each one in detail:

Part A: "*The manuscript focuses on simulating the creation of cobalt and ruthenium atom pairs (Co-SO-Ru) in biology to optimize the interface water for advanced hydrogen electrocatalysis. However, many previous studies have used atomic pairs and interface structures to enhance performance. So, this manuscript lacks novelty, and I will not recommend publication.*"

Response: We sincerely appreciate your recognition of our sulfur-oxygen bridged Ru-Co atomic pair materials as highly promising catalyst for optimizing interfacial water structure in alkaline hydrogen electrocatalysis. Following your insightful comments and the suggestions, as well as feedback from other reviewers, we have conducted additional experiments (Fig. 1b; Fig. 2a, c, e, f; Supplementary Fig. 29-34) and made substantial revisions to the manuscript. All relevant data have been incorporated to support our claims, and we have thoroughly addressed all questions and concerns in the revised manuscript and supplementary information. It is believed that these enhancements significantly improve the quality of this work. We thank you once again for your thoughtful evaluation and constructive feedback.

Regarding concerns about novelty, we would like to reiterate the motivation and conceptual framework of our study. We agree with the reviewer that atomic pairs and interface structures have been used to enhance catalytic performance. However, it is still challenging to correlate the features of atomic pairs and interface structures with the specific electrocatalytic processes, especially giving the distinct requirements of different reactions through modulation of the electrode-solution interfacial microenvironments. Therefore, the electrode interfacial microenvironments would be adjusted properly for specific electrocatalysis. In the present work, we focus on enhancing the hydrogen-bond network at the electrode interface to improve catalytic performance, rather than merely synthesizing an atomic-paired active sites.

Owing to insufficient hydrophilicity of metallic sites, the weak electrostatic interactions between metallic catalysts and interfacial water molecules would result in low connectivity within the

hydrogen-bond network (**Fig. 1R a**). Although the interface structures have been designed to enhance the catalytic performance in different fields, the active sites in these catalysts remain underutilized due to spatial limitations at the heterojunction interfaces. Therefore, precisely designing the active sites at atomic scale to manipulate the configurations of interfacial water remains a significant challenge. Our study addresses this by constructing heteroatom bridged metal sites to strengthen the hydrogen-bond networks in electrode microenvironments, achieving efficiently hydrogen oxidation and evolution reaction (HOR/HER). Specifically, we introduce a novel configuration for Ru-based electrodes by fabricating hydrophilic sulfur-oxygen (S=O) bridges between Co and Ru sites (Co_s-SO-Ru). The stereoscopic sulfur-oxygen bridges would enhance the connectivity of hydrogen-bond network to promote proton transfer and repel cations from the electrode surface (**Fig. 1R b**). This configuration would efficiently boost HOR/HER catalytic performance via regulating the adsorption-desorption of reaction intermediates. It can be observed that the Co_s-SO-Ru electrode efficiently adsorbs protons due to the favorable hydrogen-bond network, thus boosting the electrocatalytic hydrogen conversion ($H_2O + e^- \rightarrow H^* + OH^-$). Especially, during seawater splitting, the long-term catalytic stability of the Co_s-SO-Ru electrode would also demonstrate that the highly connected hydrogen-bond network would prevent the formation of insoluble precipitates, such as Ca^{2+} and Mg^{2+} cations. To further clarify the novelty of our study, we highlight the following key findings:

1) The sulfur-oxygen bridge between Co and Ru sites is challenging to achieve using traditional sulfuration strategies, which typically form metal sulfides. Herein, a "self-sulfidation" process, enabled by the counter anion (SO_4^{2-}) from $CoSO_4$ during the pyrolysis of a Co-organic precursor, facilitates the formation of S-O bonds.
2) The synergy between the organic structure and metallic active sites optimizes interfacial catalytic microenvironments to promote a robust hydrogen-bond network for efficient proton transfer, significantly enhancing electrocatalysis for HOR/HER.
3) Electron donation from Co sites reduces the surface oxophilicity of Ru, optimizing hydroxyl adsorption-desorption and ensuring timely regeneration of Ru active sites, thereby enhancing overall catalytic activity.

In distinct with previous works on atomic pairs and interface structures, our development of hydrophilic sulfo-oxygen bridges between Co and Ru sites is unprecedented. Moreover, the regulation of interfacial water configurations through heteroatom–metal synergy addresses a critical gap in heterogeneous catalytic systems. The use of self-sulfidation process in the presence of the counter anion (SO_4^{2-}) enables the successful formation of sulfo-oxygen bridged Co and Ru atomic sites, which

regulates interfacial hydrogen-bond networks and boosts HOR/HER catalytic performance. This work not only represents a novel material design but also advances the understanding and regulation of interfacial microenvironments for electrocatalysis, with broad implications for hydrogen evolution, hydrogen oxidation, CO_2 reduction, and related fields.

In the revised manuscript, we have clarified the concept and novelty of this study, and included additional data to support our claims. For example, on page 2, lines 62–65, we have added:

"***To regulate the interfacial H_2O structures, doping strategies with foreign atoms to construct atomic pairs and interface structures have been explored to enhance catalytic performance, but there are often limited by weak electrostatic interactions between metallic sites and interfacial water due to the insufficient hydrophilicity of metallic electrocatalysts.***"

The revised manuscript now effectively addresses all concerns and highlights the significant advances made in this work. We thank you again for your time and effort in reviewing our submission.

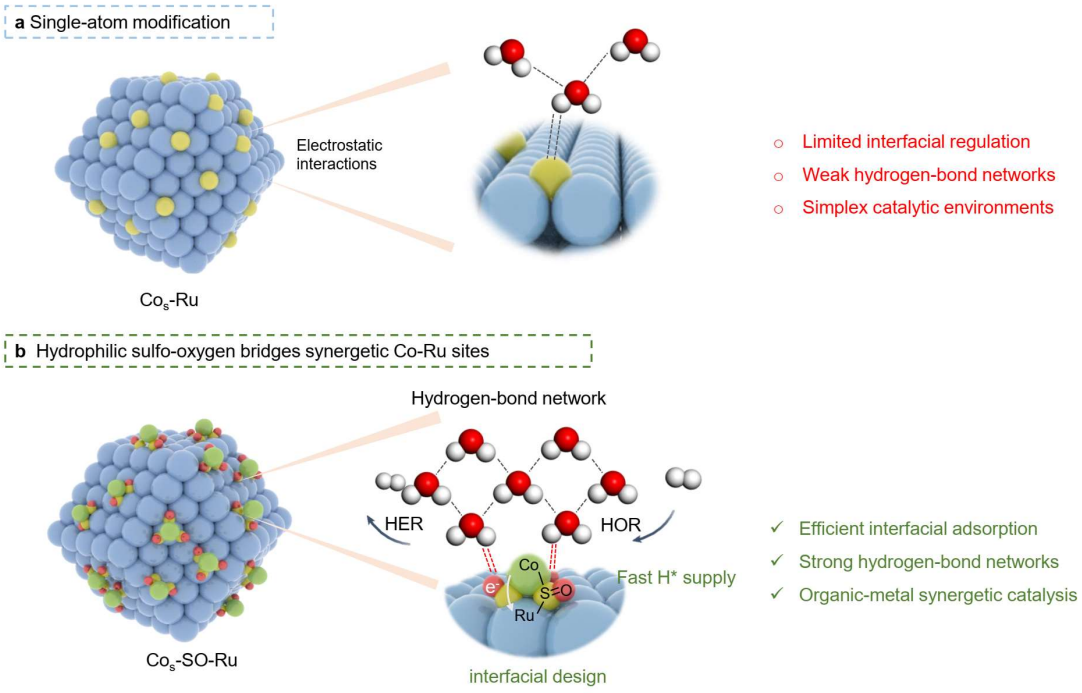


Figure. 1R Comparison of simplex atomic sites and sulfo-oxygen bridged Co-Ru sites. a The illustration of constructed atomic pairs and corresponding configuration of interfacial water. **b** The illustration of Co_s-SO-Ru active sites and induced strong hydrogen-bond networks.

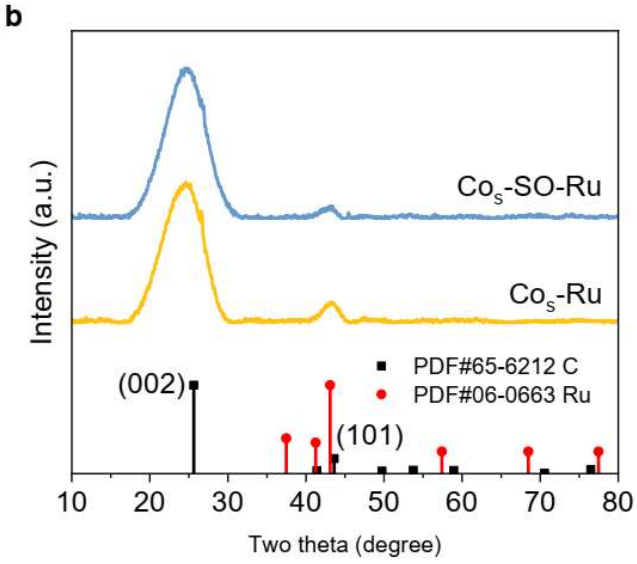


Fig.2b XRD patterns of different catalysts.

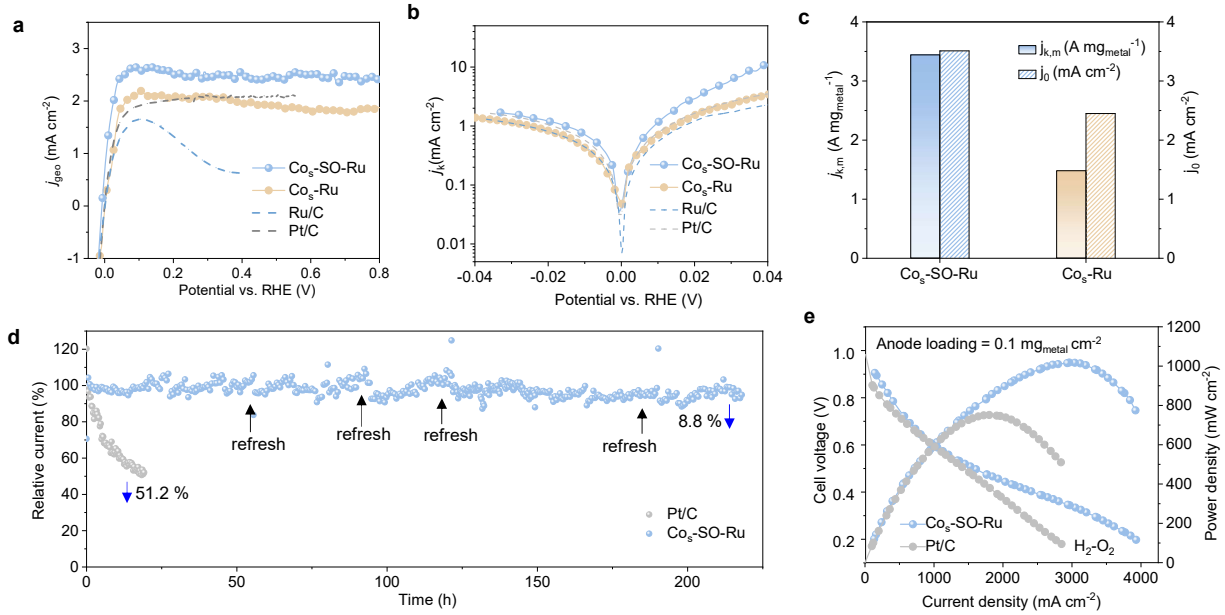


Fig. 4 Electrocatalytic analysis. a HOR curves of different catalysts in H_2-saturated 0.1 M KOH. **b** Calculated Tafel plots of the kinetic current density (j_k). **c** Comparison of kinetic mass activity ($j_{k,m}$) with an overpotential of 50 mV and exchange current density (j_0) of different catalysts. **d** Long-term stability test of different catalysts at 0.1 V. **e** Polarization and power density curves of HEMFCs using different catalysts as anode. Test conditions: Using Co_s-SO-Ru or Pt/C (0.1 mg_{Ru} cm^{-2}) as anode and Pt/C (0.4 mg_{Pt} cm^{-2}) as cathode with H_2 and O_2 flow rate of 1.0 L min^{-1}. The cell, anode, and cathode humidifier temperatures are 80, 77, and 79 °C, respectively; back pressures were symmetric at 200 kPag for both sides.

Part B: "*As for simulation biology, it is just a gimmick and not the focus of the author's work. Although the author constructed a single atom, only a simple characterization was carried out, and the performance of the entire article is mainly attributed to the atomic pairs and interface structure. The authors' claim of observing single-atom sites on the carbon support is overstated and insufficiently supported by the presented data (lines 112-114). While it is true that signal intensity in HAADF-STEM images correlates with atomic number (Z-contrast), it is crucial to acknowledge that other factors, particularly sample thickness, can significantly influence the observed intensities. The decrease in intensity may be due to the superposition of fewer atoms rather than the presence of a single atom. This fundamental ambiguity significantly undermines the validity of the author's claims regarding the distribution of Co atoms. Therefore, the presented data does not adequately support the claim of observing single-atom sites on the carbon support. Given the limitations mentioned above, the current analysis does not provide conclusive evidence for the presence of isolated atoms.*

In addition, the XRD data analysis has shortcomings. The XRD data has significant noise, and efforts can be made to improve its quality. So, the synchrotron radiation XRD (or even synchrotron radiation on the distribution function) of the material can be further performed for analysis."

Response: We sincerely thank the reviewer for the thoughtful and constructive comments on our work, as well as the professional suggestions provided. We fully acknowledge and agree with the observation that the HAADF-STEM images presented in this study do not directly demonstrate the presence of single atoms on the carbon support. It is important to clarify that our intention was never to claim the existence of single-atom sites on the carbon substrate. In contrast, the work demonstrates the presence of cobalt among Ru nanoclusters would reduce the surface oxophilicity of Ru due to the electron donation from Co sites. Especially, the stereoscopic sulfur-oxygen bridge between Co and Ru sites promotes a robust hydrogen-bond network for efficient proton transfer, significantly enhancing electrocatalysis for hydrogen oxidation and evolution reactions. To clarify this point and avoid any confusion, we have refined the corresponding discussion in the revised manuscript:

Page 2, Abstract: "***we herein demonstrate that the hydrophilic sulfo-oxygen bridging between Co and Ru sites (Co_S-SO-Ru) optimizes interfacial water structure via a favorable hydrogen-bond network, promoting hydrogen oxidation and evolution reactions.***"

Page 5, line 112-114: "***Almost no Co/Ru-S-C single-atom sites can be observed on the carbon support, as sulfur is not readily introduced into the carbon substrate. Instead, this result demonstrates that the atomic cobalt preferentially disperses on the surface of Ru nanoclusters via easily formed metal-sulfur bridge bonds (Fig. 2e-f, Supplementary Fig. 10)***"

According to your feedback, we have attempted to improve the quality of XRD results via synchrotron X-ray powder diffraction (SXPD) at BL14B1 station of Shanghai Synchrotron Radiation Facility (SSRF) with an energy of 18 keV (wavelength calculated to be 0.6888 Å). However, the data quality for both Co_s-SO-Ru and Co_s-Ru were poor, likely due to the strong fluorescence (**Fig. R2**). It should be noted that the organic-metal complexes would promote the fluorescence-emission that excited by X-ray beam (*Sci. Adv., 2023,* 9, eadh0198(2023)). To address this, we re-collected the XRD data using a Rigaku SmartLab X-ray diffractometer (9 kw) with Cu Kα radiation (2θ range of 10-80°, and the scanning rate was set as 2° min^{-1}). As exhibited in **Fig.2b**, the XRD patterns are now clear with minimal noise, and no Co-based metallic oxides or sulfides can be detected, providing solid evidence for the presence of atomically dispersed Co sites. To clarify atomic structures of Co_s-SO-Ru, the configuration of stereoscopic sulfo-oxygen bridged Co and Ru sites was further analyzed in detail:

1) The EXAFS spectrum at the Co *K*-edge reveals the predominant Co-S bonds (2.23 Å) in the first coordination shell and weaker Co-S-O bonds (2.80 Å) in the second coordination shell (**Fig. 3g**), providing solid evidence for the formation of Co-S structures. Notably, no Co-Co and Co-O-Co peaks were detected by the EXAFS spectrum, confirming the presence of mononuclear cobalt bridged via sulfo-oxygen bonds with ruthenium sites in Co_s-SO-Ru configuration.
2) XPS results demonstrate that the cobalt species with low contents in Co_s-SO-Ru efficiently regulate the electronic structures of Ru clusters. The electron transfer observed between Co species and Ru clusters suggests that Co sites are incorporated into Ru clusters rather than being deposited onto the carbon support. This phenomenon is attributed to the presence of sulfur species for forming stable metal-sulfur bonds during pyrolysis, in contrast to carbon-sulfur bonds
3) The HAADF-STEM images indicate the presence of Co sites on Ru clusters rather than carbon supports, supporting the successful construction of sulfo-oxygen-bridged Co-Ru sites in Co_s-SO-Ru. However, due to the weak signal intensity of Co species compared with Ru species, the atomically dispersed Co sites cannot be directly observed in HAADF-STEM images.

We appreciate the reviewer's thoughtful input, which has significantly improved our work. In response to the raised concerns, a couple of new results have been incorporated into the revised manuscript to provide deeper insights into the structure and electronic properties of the sulfo-oxygen-bridged Co-Ru sites. All questions and concerns have been thoroughly addressed in the revised manuscript and the response letter. With the significant revisions made and the novelty of our findings clearly articulated, we sincerely hope that this revised manuscript meets the standards for publication in *Nature Communications*.

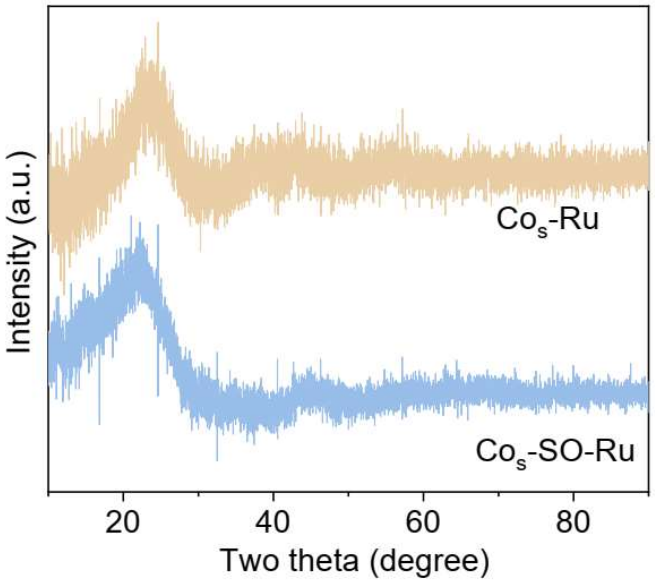


Fig. R2 The synchrotron X-ray powder diffraction (SXPD) patterns of different catalysts.

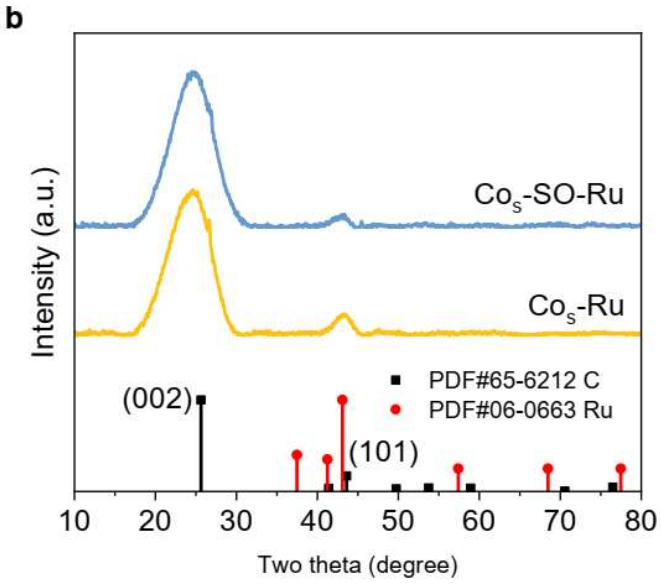


Fig.2b XRD patterns of different catalysts.

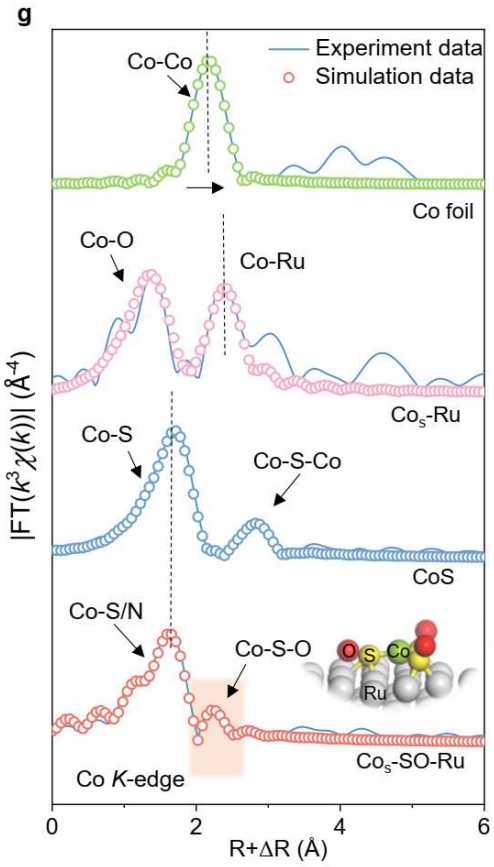


Fig. 3g EXAFS in R-space and corresponding fitting curves for Co foil, CoO, Cu_3O_4, Co_s-Ru, and Co_s-SO-Ru.

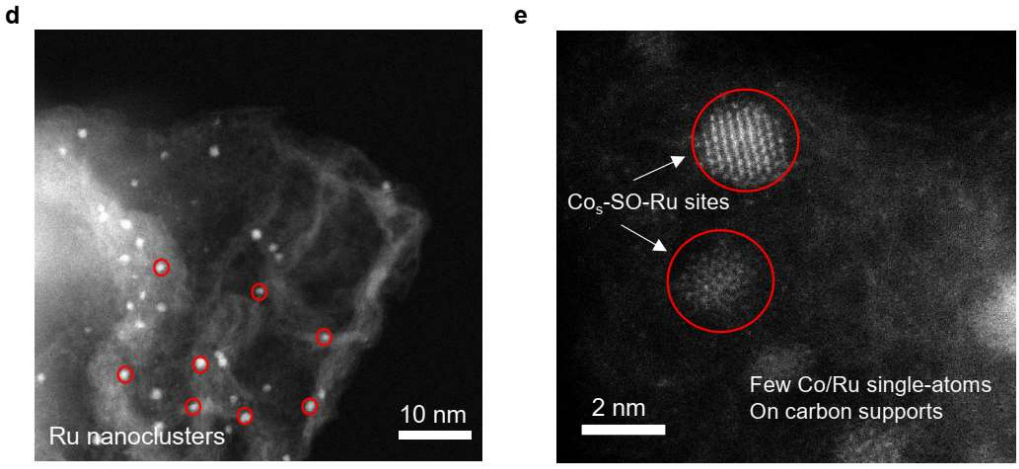


Fig. 2d HAADF-STEM images of Co_s-SO-Ru. **e** Atomic-resolution HAADF-STEM image of Co_s-SO-Ru.

Reviewer #2:

"*In this manuscript, the authors present stereoscopic sulfo-oxygen bonds bridging Co and Ru atomic pairs as highly active sites for advanced hydrogen catalysis. The Cos-SO-Ru structure demonstrates superior catalytic performance in both the hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER), surpassing commercial Ru/C and Pt/C catalysts. The authors convincingly show that the sulfo-oxygen bridges enhance the hydrogen-bond network by repelling cations from the Ru electrode surface, offering a novel approach to modulate interfacial environments at the atomic scale. These findings are significant and provide fresh insights into the development of efficient HOR catalysts. I recommend the manuscript for publication in Nature Communications, pending minor revisions as outlined below*:"

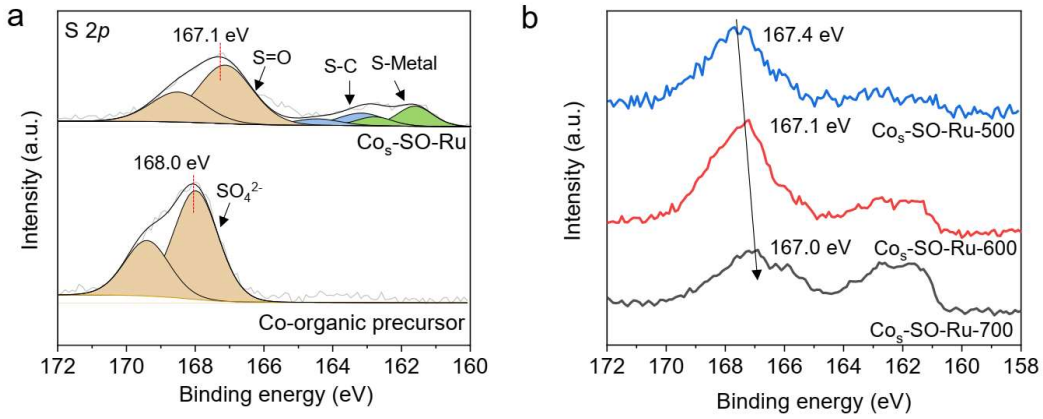
Response: We sincerely appreciate your kind support and valuable feedback. In response to your insightful comments, as well as those from other reviewers, we have conducted additional systematic experiments and refined the manuscript accordingly.

Comment 1: "*For the formation mechanism of stereoscopic sulfo-oxygen bonds, a more detailed explanation is required to strengthen the understanding of how these bonds are formed*."

Response: Thanks the reviewer for this valuable suggestion. Accordingly, the formation mechanism of stereoscopic sulfo-oxygen bonds has been carefully analyzed and discussed in revised manuscript. As exhibited in Supplementary Figure 14, the binding energy of S=O bonds shift to a lower position with increasing the carbonization temperature, indicating the deoxygenation process of SO_4^{2-} counter anion. Additionally, the decreased intensity of S=O peaks also demonstrate the reduction of SO_4^{2-} anion, likely facilitated by reductive nature of the carbon supports during pyrolysis. The concurrent increase in S-metal bonds suggests that the S=O bonds would ultimately transform into metallic sulfide. Based on the above analysis, we conclude that the deoxygenation and reduction process of the SO_4^{2-} anion are critical for the formation of S=O bonds and metal-S bonds during pyrolysis. The corresponding discussions have been incorporated into the revised manuscript and Supplementary Information, as detailed below:

Page 6, line 138-141: "***The high-resolution S 2p X-ray photoelectron spectroscopy (XPS) spectra confirm the formation of S=O bonds (167.1 eV), which would be attributed to the deoxygenation and reduction of the SO_4^{2-} anion via the "self-sulfidation" process during pyrolysis.***"

Supplementary Information, Page 16:



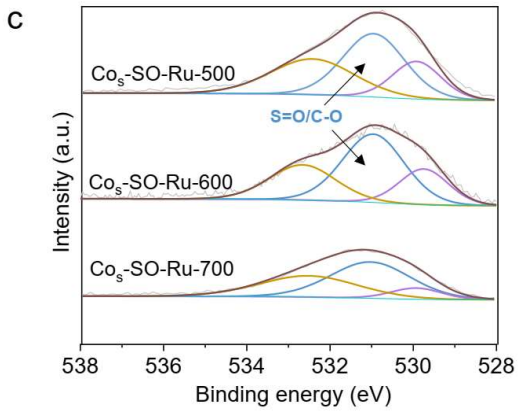
Supplementary Figure 14. a The S 2p XPS spectra of Co-organic precursor and Co_s-SO-Ru. b The S 2p XPS spectra of Co_s-SO-Ru-500/600/700.

The Co_s-SO-Ru-500/600/700 samples are obtained by pyrolyzing the Co(Ru)-organic precursor at 500, 600, and 700 °C, respectively. As shown, increasing the carbonization temperature results in a shift of the binding energy of S=O bonds to a lower position, indicating the deoxygenation process of SO_4^{2-} counter anion. Meanwhile, the decreased intensity of S=O peaks also demonstrate the reduction of SO_4^{2-} anion, which is likely facilitated by the reductive nature of the carbon support during pyrolysis. The increase in S-metal bond intensity further suggests that the S=O bonds are ultimately converted into metallic sulfide.

Comment 2: "*Please include the XPS data for oxygen elements obtained at different temperatures, aimed to clarify how temperature influences the bonding environment*."

Response: Thanks. The XPS results for oxygen elements at different carbonization temperatures have been added to Supplementary Information. As shown, the intensity of O 1*s* peaks decrease with increasing the carbonization temperature, which would be attributed to the progressive reduction of S=O bonds at higher carbonization temperatures.

Supplementary Information, Page 16:



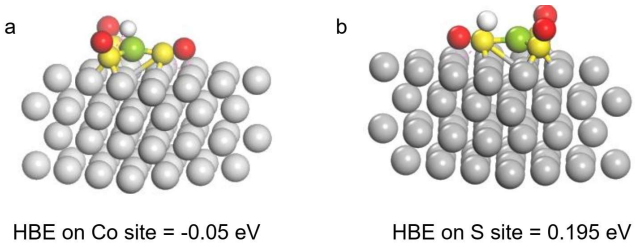
Supplementary Figure 14. c The O 1s XPS spectra of Co$_s$-SO-Ru-500/600/700.

As shown, the intensity of O 1*s* peaks decrease with increasing the carbonization temperature, which would be attributed to the progressive reduction of S=O bonds at higher carbonization temperatures.

Comment 3: "*Why Co$_s$-SO-Ru achieves optimal H* adsorption-desorption energy. Further discussion of this point would help clarify the underlying factors contributing to the enhanced catalytic activity.*"

Response: Thanks. It is worth noting that the high electronegativity of Ru (Pauling scale = 2.2) would lead to a strong adsorption capacity for protons (*Adv. Mater.* 2023, 35, 2303331.). This strong proton adsorption leads to unfavorable desorption of H* from the Ru surface, as further confirmed by theoretical calculations showing that the Ru (001) model exhibits the highest ΔG_{H^*} (-0.54 eV). Additionally, both experimental and theoretical results reveal abundant electron transfer from Co sites to Ru clusters, leading to electron-enriched Ru surfaces. These enriched electronic structures around the Ru nuclei facilitate H* desorption, thereby promoting the kinetics hydrogen-evolution reaction. The optimal H* adsorption-desorption energy on Co$_s$-SO-Ru would be attributed to the electron-enriched Ru sites, which enhance hydrogen desorption. Furthermore, the weak hydrogen binding energy on adjacent sulfur sites indicates that the S=O bonds would also contribute to the improved hydrogen desorption on neighboring Ru sites (Supplementary Figure 47). The discussions on these optimal H* adsorption-desorption behaviors have been added to the revised manuscript as follows:

Page 15, Line 325: "Besides, due to the electron-enriched Ru sites, the Gibbs free-energy diagram for hydrogen desorption on Co$_s$-SO-Ru exhibits a more optimal value (-0.22 eV), close to the thermoneutral state, indicating optimal hydrogen adsorption-desorption behaviors (Fig. 6d, Supplementary Fig. 53). ***The favorable Ru-H* desorption process is further promoted by adjacent sulfur atoms in Co$_s$-SO-Ru (Supplementary Figure 54).***"



Supplementary Figure 47. The H* binding energy on **a** Co and **b** S sites of Co_s-SO-Ru."

Comment 4: "*It would be interesting to explore whether a Co(Ru)-organic precursor with abundant hydrophilic counter anions (SO_4^{2-}) could exhibit improved HER catalytic performance, potentially due to stronger hydrogen-bond networks. If possible, this hypothesis could be tested or discussed, as it would provide key evidence of the role of hydrophilic groups in facilitating hydrogen catalysis*."

Response: Thanks. To examine the HER catalytic performance of the precursor with abundant hydrophilic counter anions (SO_4^{2-}), we prepared a comparative sample, Co(Ru)-organic precursor using $CoCl_2 \cdot 6H_2O$ as cobalt source and named as Co(Ru)-organic-$CoCl_2$. This was compared with the Co(Ru)-organic-$CoSO_4$, synthesized using $CoSO_4 \cdot 7H_2O$ as cobalt source and featuring abundant counter anions (SO_4^{2-}). Notably, the Co(Ru)-organic-$CoCl_2$, which lacks hydrophilic counter anions, limits the formation of strong hydrogen-bond networks. Then, the HER catalytic performance of both samples was evaluated in Ar-saturated 1 M KOH using a rotating disk electrode. As shown in **Fig. R3**, the Co(Ru)-organic-$CoSO_4$ shows much better HER catalytic activity, requiring only a potential of 43 mV to achieve a current density of 10 mA cm^{-2}. This result supports the hypothesis that SO_4^{2-} counter anions facilitate hydrogen supply via strong hydrogen-bond networks.

Overall, we believe that this interesting finding provides key evidence that the hydrophilic counter anions would efficiently facilitate hydrogen supply by promoting strong hydrogen-bond networks.

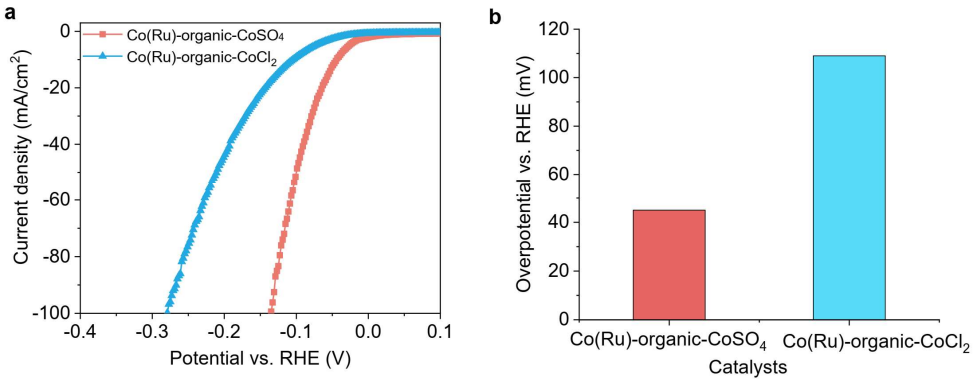


Fig. R3 a The LSV curves of different catalysts. **b** The overpotentials of different catalysts with current

density of 10 mA cm^{-2}."

Comment 5: Minor revisions: Correct the positioning of Figure 5 and amend the wording in line 323, changing "sorption" to "adsorption." Also, address any other minor errors throughout the manuscript.
Response: Thanks for your careful reading to improve the manuscript. Following your recommendations, we have carefully addressed all the minor errors throughout the manuscript,

Page 16, Line 331: "Mechanistic studies suggested that the sulfo-oxygen bridged electron donating Co atomic sites adjust the electronic structure to generate a low oxophilic Ru surface for the optimal ***adsorption*** of hydroxyl group (OH*)."

Page 9, Line 203: "***The long-term stability was examined by chronoamperometry method at 100 mV without iR corrections. The current density of Co_s-SO-Ru exhibits only a slight decrease of 8.8% after 200 h***, thus confirming the outstanding durability compared to other state-of-the-art catalysts (Fig. 4d, Supplementary Table 7)."

Page 10, Line 161: "No Co-Co and Co-O-Co peaks can be detected by EXAFS spectrum, strongly confirming ***the presence of*** mononuclear cobalt via sulfo-oxygen bridging with ruthenium sites in Co_s-SO-Ru."

Reviewer #3

"*This work is interesting and valuable, but it must address the following comments before it can be accepted*."

Response: Thank you for your kind support and valuable insights, which have greatly contributed to improving our manuscript. We have thoroughly addressed all the concerns raised and made significant revisions to enhance the overall quality of the work.

Comment 1: "*Fig.3a, the S2p fitting has some problem, please redo it and explain*."

Response: In response to the reviewer's valuable comment, we have carefully revised the S 2p fitting curves. The high-resolution S 2*p* XPS spectra confirm the formation of S=O bonds (167.1 eV) with a contents ratio of 75.2%, indicating the facile formation of sulfo-oxygen bridges in Co_s-SO-Ru. Additionally, the peaks at 163.3 and 161.5 eV are assigned to the S-Ru/Co and S-C bonds, respectively. The weak S-C peak confirms that the sulfur is rarely doped into carbon substrate, while the

coordination with cobalt readily forms via the atomic Co-S structure in Co_s-SO-Ru. The corresponding discussions have been included in the revised manuscript:

Page 6, line 138: "***The high-resolution S 2p X-ray photoelectron spectroscopy (XPS) spectra confirm the formation of S=O bonds (167.1 eV), which stems from the deoxygenation and reduction of the SO_4^{2-} anion via the self-sulfidation process during pyrolysis. The peaks at 161.5 and 163.3 eV can be attributed to the bonds of sulfur with Ru/Co and carbon, respectively*** (Fig. 3a and Supplementary Fig. 14a, b). The weak binding peak demonstrates that sulfur is rarely introduced into the carbon substrate, but the coordination with cobalt would be easily formed through the atomic structure of Co-S in Co_s-SO-Ru."

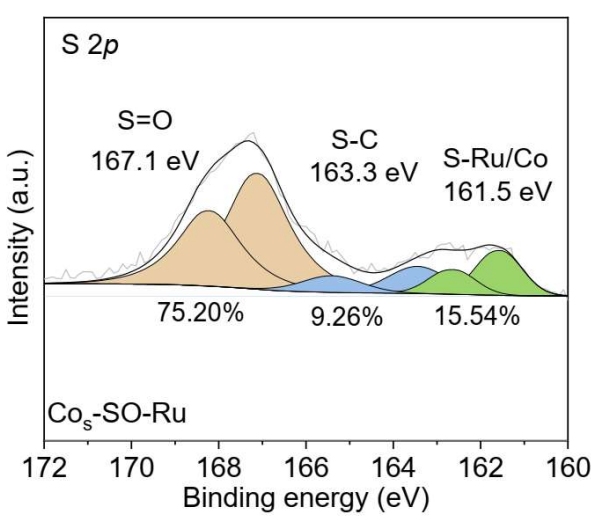


Fig. 3 a XPS spectra of Co_s-SO-Ru in S 2p regions."

Comment 2: "*for the long-term stability test by CP at 50 mV. what do you mean 50 mV? also the Cos-SO-Ru decreases 12% in 10 h, which is poor catalyst. moreover, the Pt/C is worse, which is also very weird*."

Response: Thanks for the reviewer of this valuable comment. We sincerely apologize for the oversight. The long-term stability test was conducted using the chronoamperometry method at an oxidative potential of 50 mV, rather than the chronopotentiometry method as previously stated. The corresponding revisions have been incorporated into the manuscript:

Page 9, line 204: "***The long-term stability was examined by chronoamperometry method at 100 mV without iR corrections. The current density of Co_s-SO-Ru exhibits only a slight decrease of 8.8% after 200 h,*** thus confirming the outstanding durability compared to other state-of-the-art catalysts (Fig. 4d, Supplementary Table 7)."

The observed decline in stability of Co_s-SO-Ru may be attributed to the detachment of the catalyst from the glass carbon electrode. In light of your insightful feedback in ***Comment 3***, we have also evaluated the stability of the catalysts on carbon cloth in H_2-saturated 0.1 M KOH. To further evaluate the long-term durability of Co_s-SO-Ru, the test was conducted at a higher oxidation potential of 100 mV. Additionally, the poor catalytic durability of Pt/C during HOR may stem from the oxidation of Pt sites, which has also been demonstrated in previously reported works. To ensure the reliability of our experimental results, we have carefully tested the long-term stability of Co_s-SO-Ru and Pt/C again. The corresponding results and detailed explanations are shown in Response to ***Comment 3***.

Comment 3. "*The long-term stability at small current density for 10 h is meaningless to me. We usually run 1000 h for high current density*."

Response: We sincerely appreciate your valuable feedback to improve the manuscript. In line with your recommendations, the HOR stability of Co_s-SO-Ru has been evaluated by chronoamperometry method. **Fig. 3e** exhibits the chronoamperometry response of Co_s-SO-Ru and commercial Pt/C on carbon cloth in H_2-saturated 0.1 M KOH with an oxidation potential of 100 mV. The relative current of Co_s-SO-Ru exhibits around 8.8% decrease from the initial current density after 200 h of operation. In contrast, the current density of commercial Pt/C decreases rapidly by 51.2% after just 20 h, likely due to the oxidation of Pt surface at an oxidation potential. We have also summarized the HOR durability of various state-of-the-art catalysts for comparison. As shown in **Supplementary Table 7**, the Co_s-SO-Ru presents superior durability compared to other noble-metal-based electrocatalysts, demonstrating the stable active structure of sulfur-oxygen bridged Co-Ru sites.

To gain deeper insights into the catalytic durability of Co_s-SO-Ru catalyst, the spent catalyst after 200 h HOR test was collected and characterized via XPS and STEM. The corresponding results and discussions are provided in the manuscript and supplementary information:

Page 9, line 201-212: "***The long-term stability was examined by chronoamperometry method at 100 mV without iR corrections. The current density of Co_s-SO-Ru exhibits only a slight decrease of 8.8% after 200 h,*** thus confirming the outstanding durability compared to other state-of-the-art catalysts (Fig. 4d, Supplementary Table 7). ***The TEM and HAADF-STEM images revealed that the spent catalyst retains similar structures and nearly unchanged size of Ru clusters (~ 1 nm) compared with the pristine Co_s-SO-Ru (Supplementary Figure 30,32), demonstrating the stable structure. The EDS mapping exhibits the homogenous dispersion of sulfur and oxygen atoms in Co_s-SO-Ru after 200 h of operation (Supplementary Figure 33). The XPS analysis further confirms that the S=O and S-Ru/Co bonds remain well-preserved (Supplementary Figure 34), indicating the structural***

robustness of S=O bridges in Co_s-SO-Ru. Additionally, the Ru sites also maintain a stable valence state under the oxidation potential after 200 h of testing (Supplementary Figure 35). Overall, these experimental results confirm the stable chemical states of Co_s-SO-Ru."

Thank you again for your valuable comments to improve the quality of our work. Different from HER performed under reduction potential, achieving 1000 h of testing for HOR under oxidation potentials is more challenging. As exhibited in Supplementary Table 7, most advanced HOR catalysts cannot exhibit the same level of durability like HER electrocatalysts, because the OH^- would occupy the active metal sites under oxidation potentials. Meanwhile, the continuous H_2 supply (300 mL/min) needs harsh laboratory conditions that limit the ultra-long stability test. Our chronoamperometry tests conducted over 200 h and the corresponding characterizations of spent catalyst provide sufficient evidence to confirm the good stability and catalytic performance of Co_s-SO-Ru in comparison with most previously reported state-of-the-art catalysts (Supplementary Table 7). Besides, this work mainly focuses on understanding the stereoscopic sulfo-oxygen bridges enhanced the connectivity of hydrogen-bond network for promoting the proton transfer process. Therefore, we hope that the reviewer will find the stability of the Co_s-SO-Ru catalyst acceptable, even without the 1000 h HOR test.

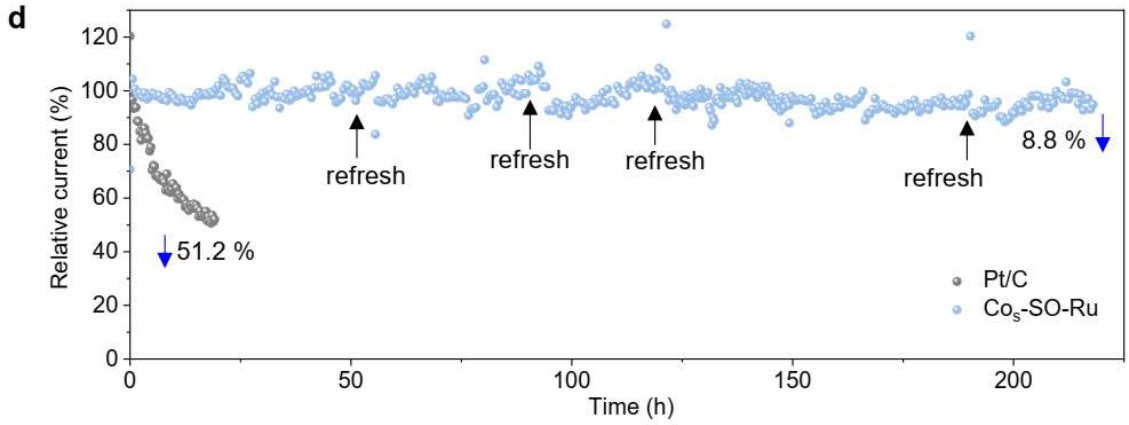


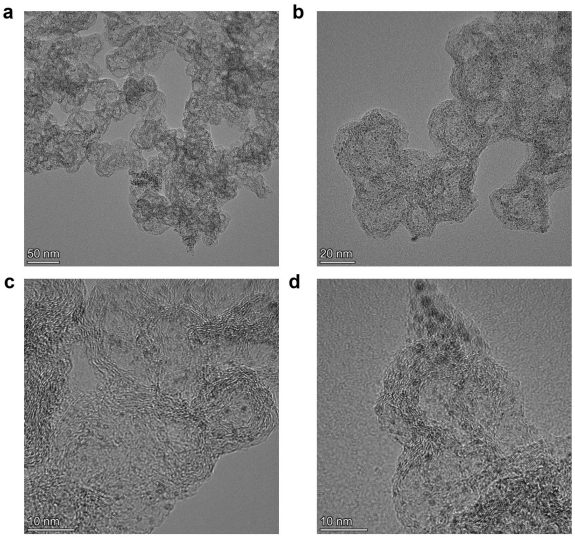
Fig.3d Stability test of different catalysts with an oxidation potential of 100 mV.

Supplementary Table 7. *Comparison of long-term HOR stability of Co_s-SO-Ru with various recently reported state-of-the-art noble-metal-based catalysts in 0.1 M KOH.*

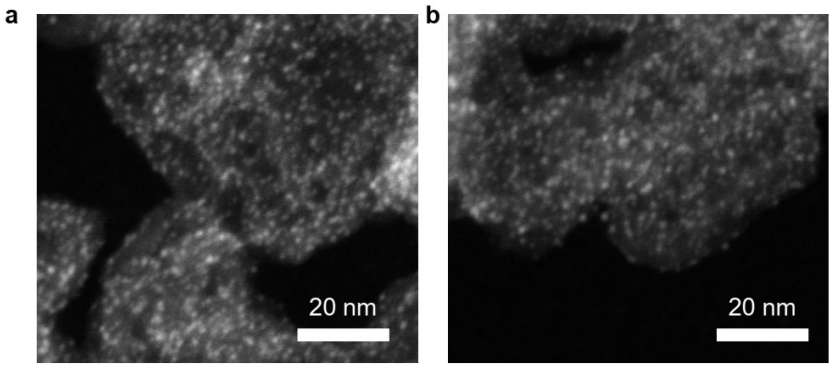
Catalysts	*Reaction time (h)*	*Decreased activity (%)*	*Reference*
Co_s-SO-Ru	*200*	*8.8*	*This work*

Ir_{SA}-Mo_2C/C	120	~5	*Nat. Commun. 15, 4236 (2024).*
Ru@TiO_2	100	10.6	*Nat. Catal. 3, 454–462 (2020).*
Ru-WC_x	40	6.63	*Angew. Chem. Int. Ed. 2023, 62, e202311937.*
Ni/V_2O_3	16	1.5%	*Angew. Chem. Int. Ed. 2023, 62, e202217275*
$Mn_1O_x(OH)_y$@ Ru/C	3	11.30	*J. Am. Chem. Soc. 2024 146 (24), 16619-16629*
2H-Pd@2H-NiRh NRs	10	16	*J. Am. Chem. Soc. 2024, 146, 24141-24149*
Ru–$Cr_1(OH)_x$	50	12	*Nat. Commun. 13, 5894 (2022).*
Ru/VOC	3	9.3	*J. Am. Chem. Soc. 2023, 145, 27867-27876*
HEA	1	19	*Angew. Chem. Int. Ed. 2023, e202217976*
$Co_{0.2}Ru_{0.7}Pt_{0.1}$/ PNC	1	14.20	*Angew. Chem. Int. Ed. 2023, e202306881*
i-ZnIn-PR	2.778	6.1	*Nat. Commun. 15, 1097 (2024)*
Ru-MnO/C	1	8.6	*Adv. Energy Mater. 2024, 2404266.*
$(RuCo)_{NC+SAs}$/ N-CNT	10	14.7	*Angew. Chem. Int. Ed. 2024, 63, e202404761.*
$fcc_{0.42}$ Ru-Sn	14	35	*Energy Environ. Sci., 2024,17, 5922-5930*
Ru/RuO_2-180	8	10	*Adv. Mater. 2023, 35, 2208821.*

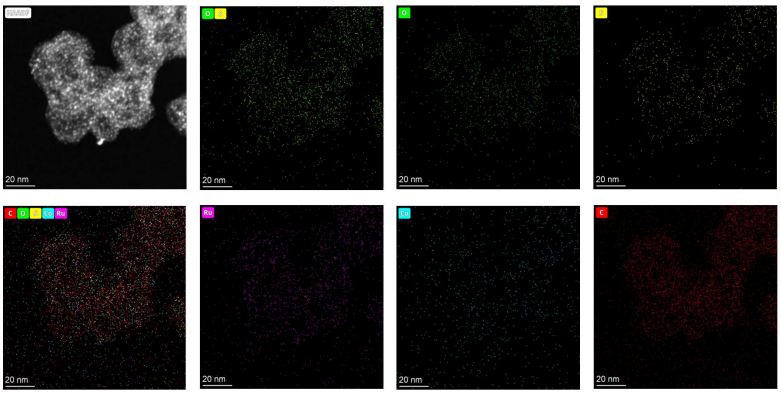
Supplementary Information, Page 15:



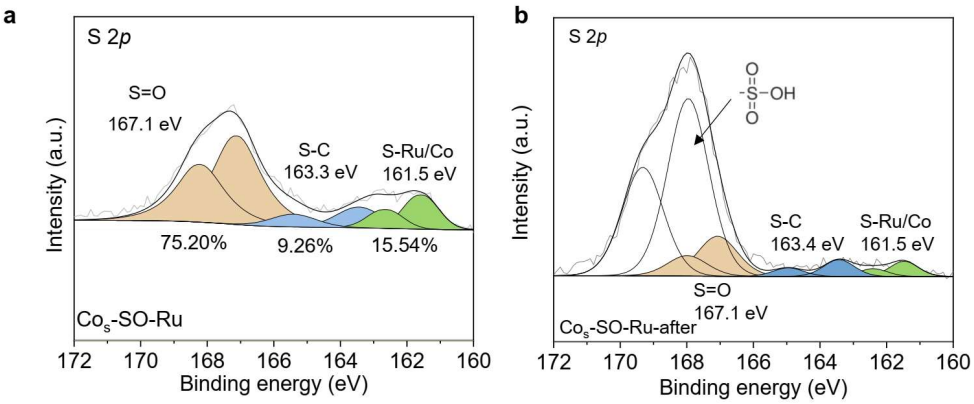
Supplementary Figure 29. TEM images of the nanocarbon-supported Co_s-SO-Ru-after.



Supplementary Figure 30. HAADF-STEM images of the nanocarbon-supported Co_s-SO-Ru-after.

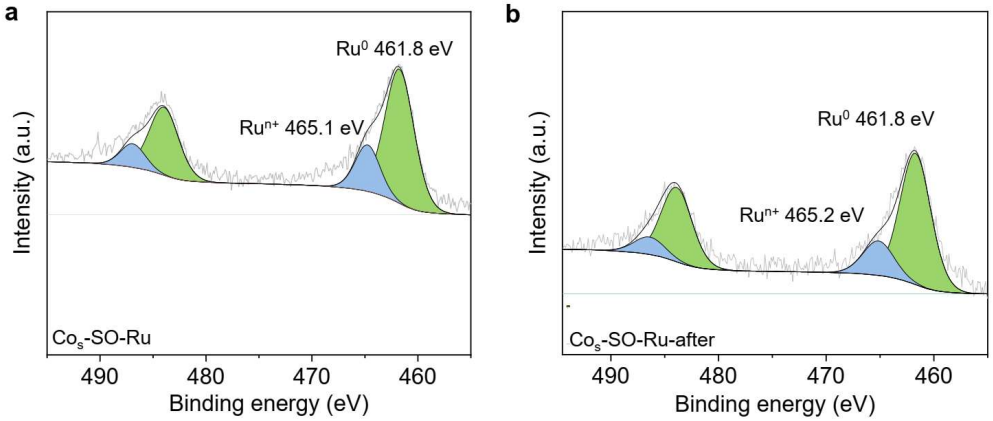


Supplementary Figure 31. HAADF-STEM image of Co_s-SO-Ru-after and corresponding EDX mappings.



Supplementary Figure 32. XPS spectra of a Co_s-SO-Ru and b Co_s-SO-Ru-after in S 2p regions.

It should be note that the strong peak at 168.1 eV would be attributed to presence of -SO_3H groups due to the Nafion polymers covering on the surface of catalysts.



Supplementary Figure 33. XPS spectra of a Co_s-SO-Ru and b Co_s-SO-Ru-after in Ru 3p regions.

Comment 4 "*The catalyst for HOR in a real fuel cell test is recommended.*"

Response: Thanks. Owing to the outstanding HOR performance of Co_s-SO-Ru, we then tested it as the anode catalyst for hydroxide exchange membrane fuel cell (HEMFC). As exhibited in Fig.4e, the Co_s-SO-Ru presents a peak power density of 1.02 W cm^{-2} at 2.96 A cm^{-2}, outperforming the Pt/C anode with power density of 0.75 W cm^{-2} at 1.84 A cm^{-2}. Besides, the Co_s-SO-Ru also display superior stability with only a 0.1 V voltage increase after 40 h of operation, demonstrating the great potential for practiacl applications. The corresponding results and discussions are provided in the manuscript and supplementary information:

Page 10, line 216: "***Encouraged by the remarkable HOR catalytic performance of Co_s-SO-Ru, the membrane electrode assembly was fabricated using Co_s-SO-Ru or Pt/C (0.1 mg_{Ru} cm^{-2}) as the anode and Pt/C (0.4 mg_{Pt} cm^{-2}) as the cathode. Fig. 4e illustrates that the Co_s-SO-Ru achieves a peak power density of 1.02 W cm^{-2} at a current density of 2.96 A cm^{-2}, surpassing the performance of the Pt/C anode, which exhibits a power density of 0.75 W cm^{-2} at 1.84 A cm^{-2}. Additionally, the Co_s-SO-Ru display superior stability with a 0.1 V voltage increase after 40 h of operation (Supplementary Fig. 34), demonstrating the great potential for practiacl applications.***

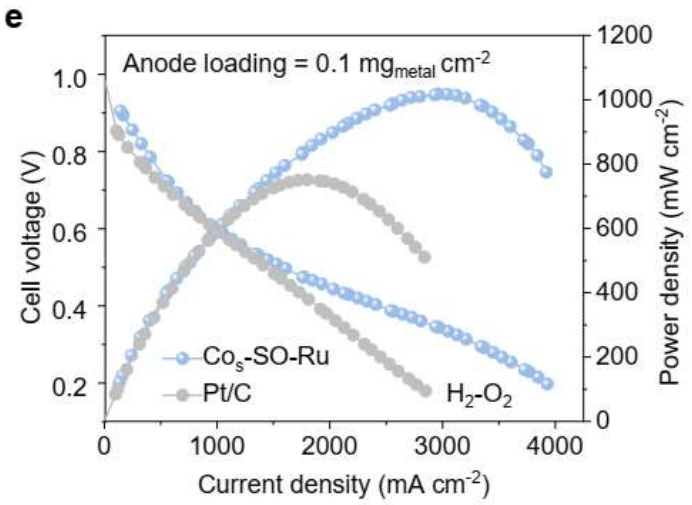
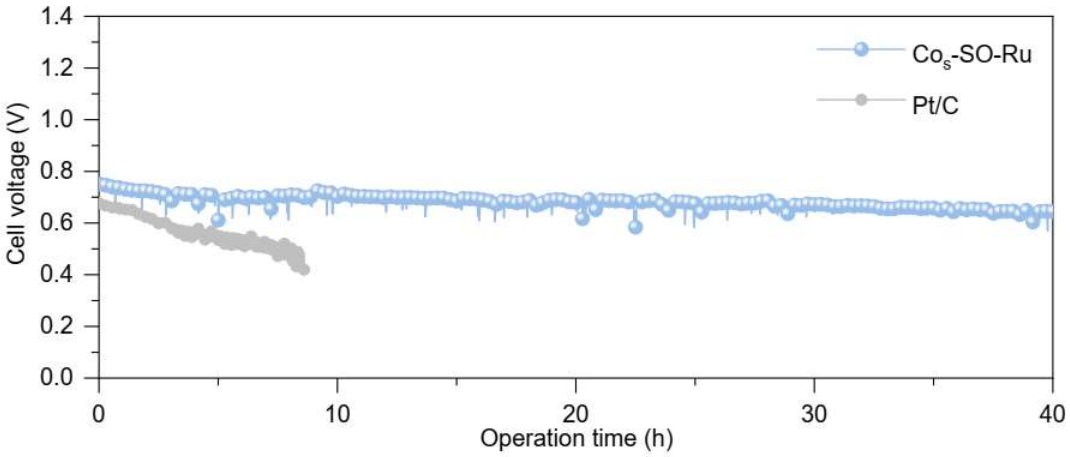


Fig. 4e Polarization and power density curves of HEMFCs using different catalysts as anode. Test conditions: Using Co_s-SO-Ru or Pt/C (0.1 mg_{Ru} cm^{-2}) as anode and Pt/C (0.4 mg_{Pt} cm^{-2}) as cathode with H_2 and O_2 flow rate of 1.0 L min^{-1}. The cell, anode, and cathode humidifier temperatures are 80, 77, and 79 °C, respectively; back pressures were symmetric at 200 kPag for both sides.

Supplementary Information, Page 36:



Supplementary Figure 34. The long-term durability test for HEMFCs using Co_s-SO-Ru or Pt/C as anode with current density of 500 mA cm^{-2}."

Comment 5 "*Why alkaline and seawater conditions were used? I did not see any comparison*."

Response: Thanks. The HER catalytic performance of Co_s-SO-Ru for seawater splitting is provided in Page 13, line 264. During seawater splitting, the accumulated cations, such as Ca^{2+} and Mg^{2+} would lead to the rapid formation of insoluble precipitates (e.g., $Ca(OH)_2$, $Mg(OH)_2$) due to the elevated pH

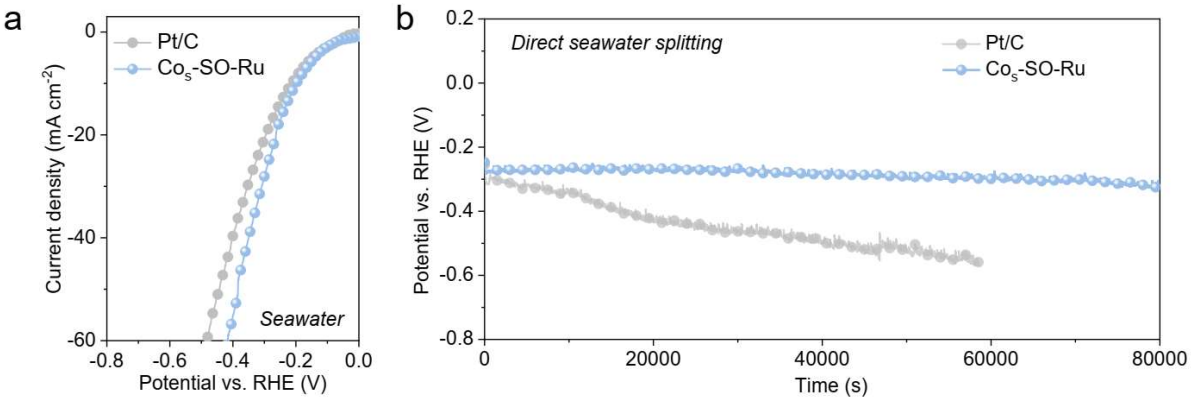
at the electrode-liquid interface (*Adv. Mater.* 2023, 35, 2303331; *Nat Commun* **15**, 9462 (2024).). These precipitates can significantly hinder catalytic activity. To demonstrate the role of strong hydrogen-bond networks in mitigating these challenges, we evaluated the HER catalytic performance of Co_s-SO-Ru in seawater. As shown in Supplementary Figure 39, the Co_s-SO-Ru showed remarkable stability, with negligible activity decay after 80,000 s, and only a slight increase in overpotential of 24 mV, indicating its strong anti-poisoning capability for seawater splitting.

To improve the logical flow and readability of this manuscript, the discussions on seawater splitting have been incorporate into the revised text:

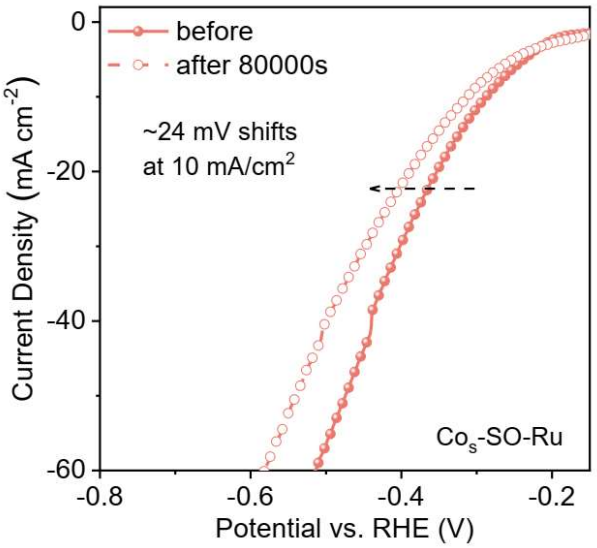
Page 9, line 234: "***The electrocatalytic performance for hydrogen evolution was evaluated under alkaline conditions with real-time iR correction (details in Methods).***"

Page 13, line 297: "***During seawater splitting, the accumulation of cations, such as Ca^{2+} and Mg^{2+}, would also lead to the rapid formation of insoluble precipitates at the electrode-liquid interface, suppressing the catalytic activity. To address these challenges, the HER catalytic performance of Co_s-SO-Ru was tested in seawater.*** Impressively, the Co_s-SO-Ru exhibited negligible activity decay after 80,000 s, with only a 24 mV increase in overpotential, indicating its anti-poisoning capability for seawater splitting (Supplementary Figs. 39, 40). Under seawater conditions, the stereoscopic -S=O bridges in Co_s-SO-Ru enable the formation of a strongly bonded interfacial hydrogen-bond network, which would alleviate the accumulation of Ca^{2+} and Mg^{2+} cations at the active interface. This reduction in cation concentration at the electrode-liquid interface prevents the formation of insoluble precipitates (e.g., $Ca(OH)_2$, $Mg(OH)_2$), thus enhancing the long-term catalytic stability of the Co_s-SO-Ru electrode."

Supplementary Information, Page 40:



Supplementary Figure 46. a HER curves of different catalysts in seawater conditions. **b** Chronopotentiometric curves for direct seawater dissociation.



Supplementary Figure 47. The LSV curves of Co_s-SO-Ru before and after long-term tests in seawater condition.

Comment 6 "*It seems the HER current start before 0 V vs. RHE for some catalysts. please explain. Also, a high current density comparison is required.*"

Response:

Thanks for the reviewer of this valuable comment. The reduction current before 0 V can be explained by the hydrogen underpotential deposition (H_{UPD}) due to the feasible proton supply onto Ru sites in alkaline conditions. As shown in the H_{UPD} tests (Fig. 4g), the Co_s-SO-Ru exhibits a well-resolved H_{UPD} peak at 0.02 V, which is more pronounced compared to Co_s-Ru. This indicates the enhanced adsorption of active hydrogen species (H*). This phenomenon can be attributed to the strong hydrogen-bond networks at the interfacial of Co_s-SO-Ru electrode, which facilitate the water splitting and proton supply to the Ru sites. However, since the thermodynamic electrode potentials for the hydrogen oxidation and evolution reaction (HOR/HER) are at 0 V (vs. the reversible hydrogen electrode), thereby, we believe that the reduction current observed before 0 V is due to the active H* adsorption on Ru sites, rather than the H_2 release. We appreciate your thoughtful input, which has been instrumental in refining our work. In response to your suggestions, the comparison of HER catalytic perfomance at high current density have been added in Supplementary Information:

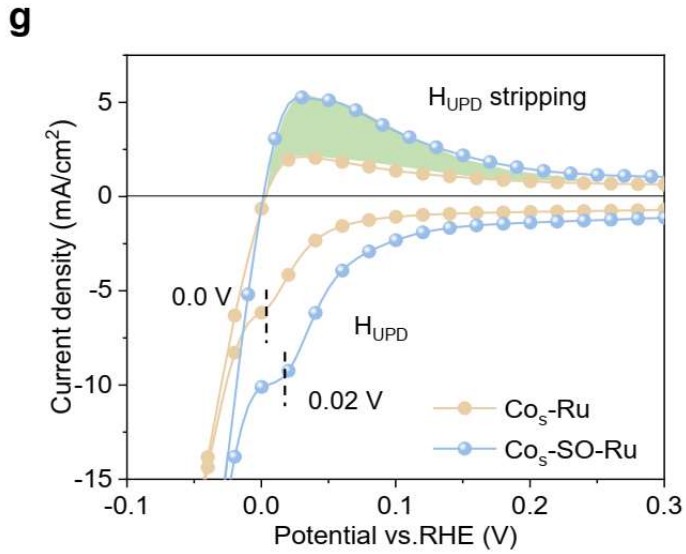
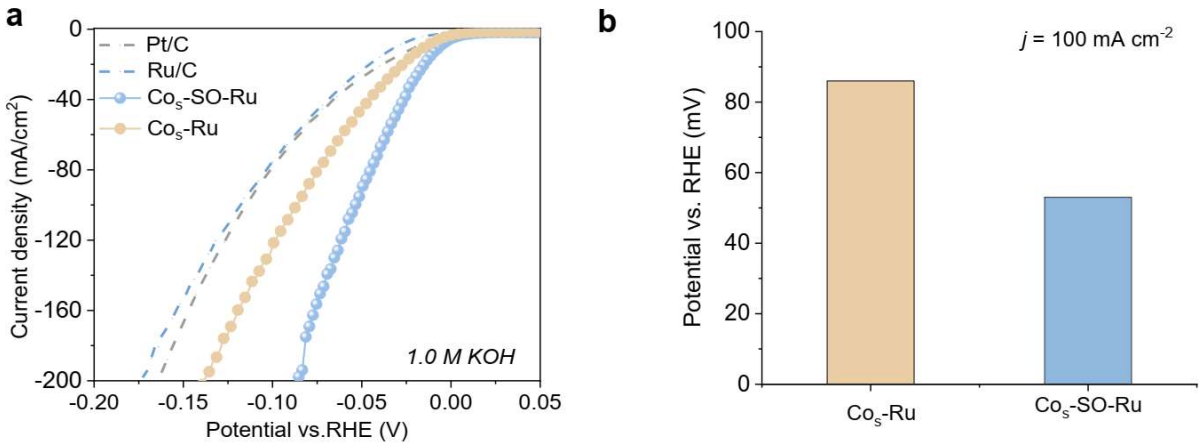


Fig. 4g Comparison of H* adsorption behavior of different catalysts in alkaline condition.

Supplementary Information, Page 31:



Supplementary Figure 36. a Comparison of HER polarization curves of different catalysts in 1.0 M KOH. b The overpotentials of different catalysts at a current density of -100 mA cm^{-2}. As exhibited, the Co_s-SO-Ru exhibits superior HER catalytic activity at high current of -100 mA cm^{-2} when compared with Co_s-Ru, Ru/C, and Pt/C.

Reviewer #4

Yang et al. have investigated how sulfur oxygen bridges optimize the role of interfacial water in alkaline hydrogen electrocatalysis in alkaline electrolytes. The efforts to carry out this work are commendable for the fast-growing field of alkaline hydrogen electrocatalysis. However, after addressing my comments, the work could be published in the prestigious Nature Communications.

Response: We sincerely appreciate your kind recognition. Accordingly, we have conducted additional experiments and thoroughly refined the content in the revised manuscript and supplementary information.

Comment 1: "*As the focus of the paper is on alkaline HOR, The tile should read "Sulfo-oxygen bridges optimize interfacial water for alkaline hydrogen oxidation/evolution reactions*"".

Response: Thanks for the reviewer of this valuable comment. To improve the logical flow and readability of this manuscript, we have revised the title to: "***Sulfo-oxygen Bridges Optimize Interfacial Water for Alkaline Hydrogen Oxidation/evolution Reactions***"

Comment 2: "*Page 3, Introduction Line 46-47, " Efficient conversion between hydrogen evolution and oxidation reactions (HER and HOR) is of importance in achieving a sustainable hydrogen economy...." This is unclear. Proofread the manuscript throughout to enhance clarity*."

Response: Thanks for the careful reading. We have carefully revised the manuscript to improve clarity and readability. The following changes have been made:

Page 3, Line 47: "***The sustainable hydrogen cycle has been considered as a viable strategy to reduce the consume of fossil fuels[1,2]. Compared with proton exchange membrane fuel cells, hydroxide exchange membrane fuel cell (AEMFC) and water electrolysis (AEMWE) technologies are attractive for renewable hydrogen economy[3-5], which allow for exploring cost-effective non-platinum catalysts for efficient hydrogen evolution and oxidation reactions (HER and HOR)[6-8]***"

Page 9, Line 204: "***The long-term stability was examined by chronoamperometry at 100 mV without iR correction, and the current density of Co_s-SO-Ru exhibits only a slight decrease of 8.8% after 200 h,*** thus confirming the outstanding durability (Fig. 4e, f)."

Page 9, Line 234: "***The electrocatalytic performance for hydrogen evolution was evaluated in alkaline conditions with real-time iR correction (details in Methods)***"

Page 13, Line 307: "***Additionally, the sulfo-oxygen bridged Co atoms decrease the oxophilicity of Ru nanoclusters***"

Comment 3: "*Ruthenium is a noble metal, could authors use non-precious metals such as Ni instead of Ru? Is this idea still valid? The control experiment with Ni should be included*."

Response: Thank you for your insightful comments and helpful suggestions. To expand the scope to non-noble metal-based catalysts, the Ni species was used to substitute Ru elemental during materials preparation. As exhibited in **Fig. R4**, the CoNi-SO/C showed higher HER catalytic performance than that of Co-SO/C, indicating that the Ni sites could also enhance the catalytic activity. Besides, the Ni-SO/C catalyst was prepared using $NiSO_4 \cdot 6H_2O$ as Ni source, which show higher HER activity than that of Ni/C using $Ni(NO_3)_2 \cdot 6H_2O$ as Ni source. Therefore, this result solidly demonstrates that the S=O species would benefit the water splitting on Ni sites in alkaline condition. However, during HOR, the CoNi-SO/C exhibit unsatisfactory catalytic performance (**Fig. R5**), which would be attributed to the formation of bulk NiCo particles, as evidenced by the XRD results (**Fig. R6**). For CoNi-SO/C, the SO_4^{2-} counter ions would be easily converted into CoNi-based sulfide, rather than forming sulfur-oxygen bonds, which also contributes to the poor HOR catalytic performance.

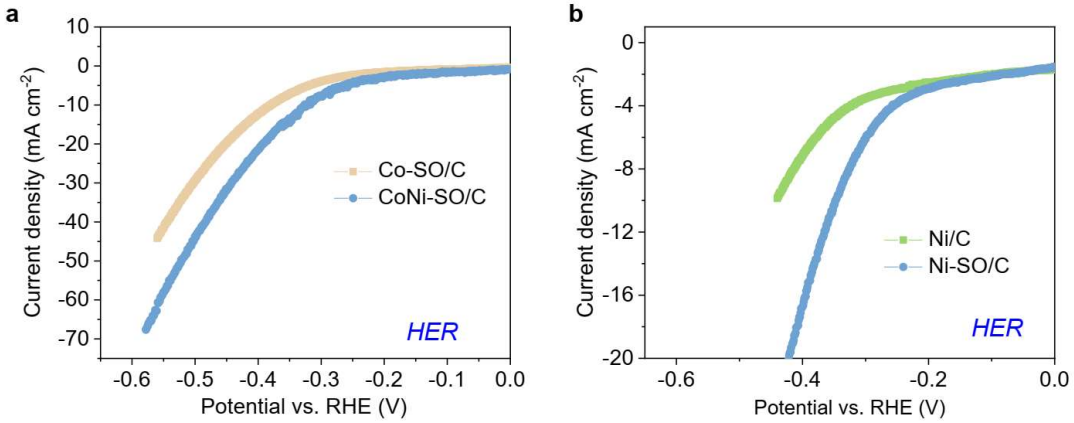


Fig. R4 a The HER polarization curves of Co-SO/C and CoNi-SO/C. **b** The HER polarization curves of Ni/C and Ni-SO/C.

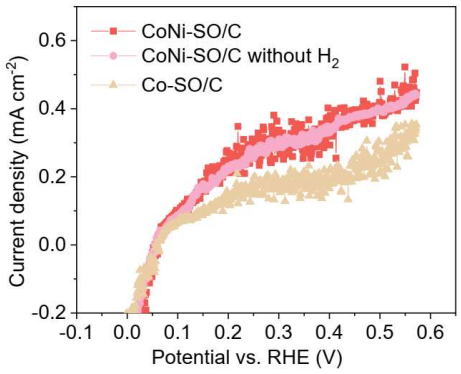


Fig. R5 The HOR polarization curves of Co-SO/C and CoNi-SO/C.

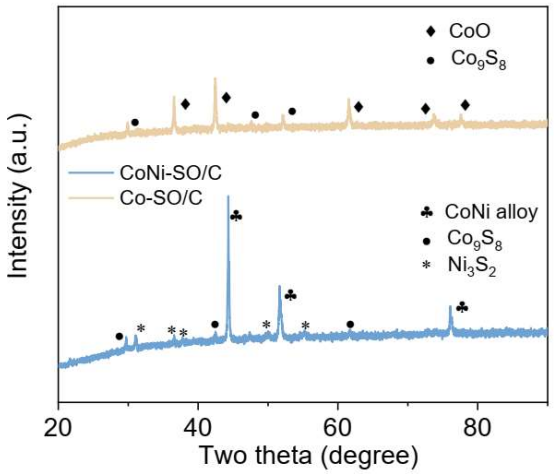


Fig. R6 The XRD patterns of CoNi-SO/C and Co-SO/C.

Comment 4: "*The Co_s-SO-Ru system is characterized in depth, especially the in-situ ATR-FTIR, XANES, and DFT investigation, and shows a strong bonding with water which is nice. How can we prove its direct effects on the HOR or HER?*"

Response: Thanks. The hydrogen underpotential deposition (H_{UPD}) tests via cyclic voltammetry (CV) curves demonstrate that the Co_s-SO-Ru exhibits a more intensive H_{UPD} peak in comparison to Co_s-Ru (Fig. 4g). This indicates that a larger number of active hydrogen species (H*) would be adsorbed onto Ru sites before reaching 0 V (RHE). Therefore, the strong hydrogen-bond networks would facilitate the proton supply, thus promoting the reaction kinetics during HER/HOR. Additionally, we also demonstrate that the hydrogen-bond networks can repel cations at the electrode-liquid interface. Cation solvation sheath effects can disrupt both H_2O* adsorption on electrode and the proton supply. During seawater splitting, the accumulation of cations, such as Ca^{2+} and Mg^{2+}, would lead to the rapid formation of insoluble precipitates at the electrode-liquid interface, thus suppressing the catalytic

durability. To verify whether the strong hydrogen-bond networks can effectively repel these cations, we tested the catalytic stability of Co_s-SO-Ru during seawater splitting (Supplementary Figure 39). The results showed negligible activity decay after 80,000 s, with only a 24 mV increase in overpotential, indicating its anti-poisoning capability in seawater splitting. This can be attributed to the ability of strong hydrogen-bond networks to alleviate the accumulation of Ca^{2+} and Mg^{2+} cations at the active interface. Finally, we prepared the Co(Ru)-organic precursor using $CoCl_2 \cdot 6H_2O$ as cobalt source, named as Co(Ru)-organic-$CoCl_2$. In comparison with the Co(Ru)-organic-$CoSO_4$ with abundant counter anions (SO_4^{2-}) prepared using $CoSO_4 \cdot 7H_2O$ as cobalt source, the Co(Ru)-organic-$CoCl_2$ lacks these hydrophilic counter anions, thus limiting the formation of strong hydrogen-bond networks. As expected, the Co(Ru)-organic-$CoSO_4$ with abundant SO_4^{2-} anions exhibited much better HER catalytic performance. This supports the conclusion that strong hydrogen-bond network would enhance the HER catalytic activity.

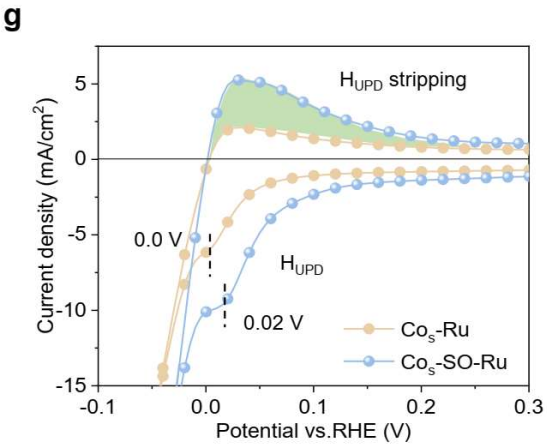
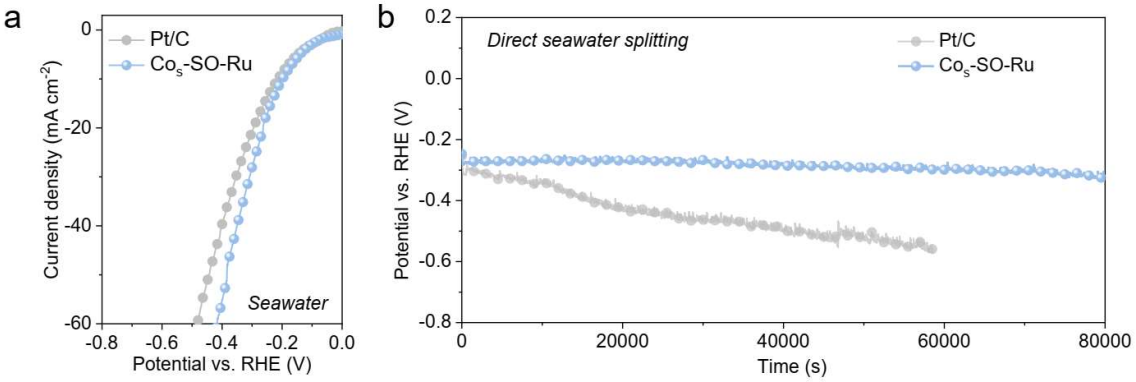


Fig. 4g Comparison of H* adsorption behavior of different catalysts in alkaline condition.



Supplementary Figure 39. a HER curves of different catalysts in seawater conditions. **b** Chronopotentiometric curves for direct seawater dissociation.

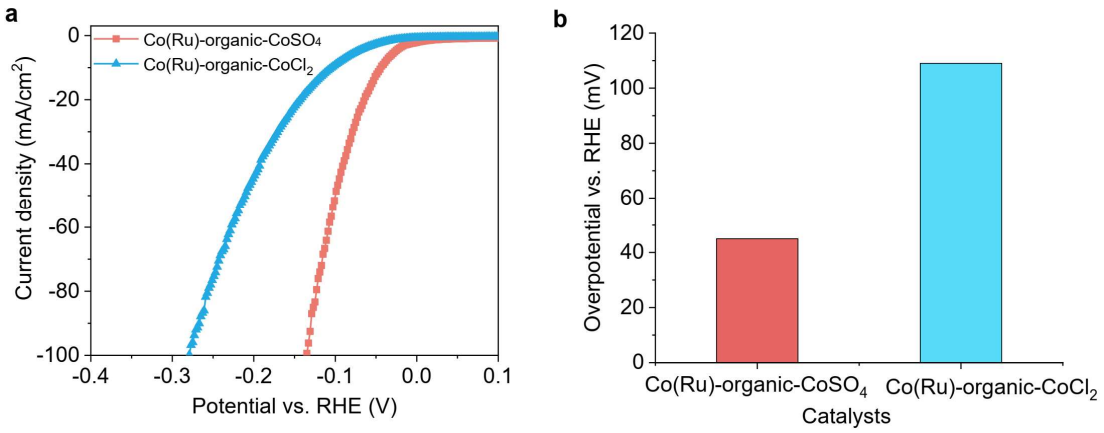


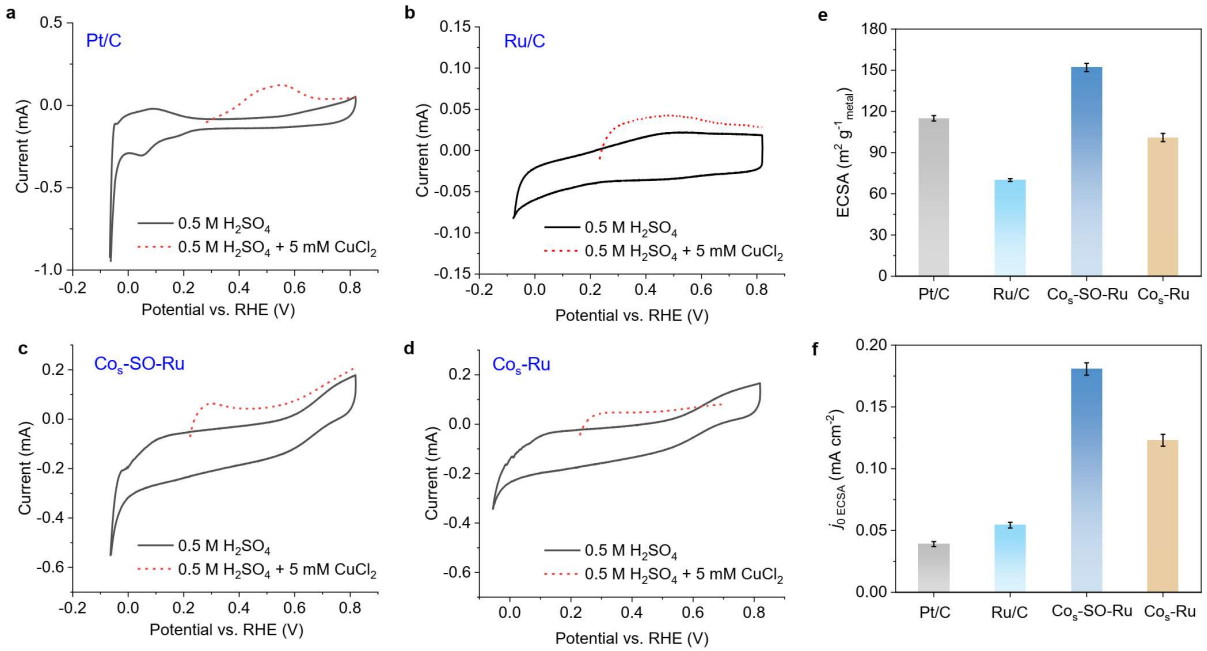
Fig. R4 a The LSV curves of different catalysts. **b** The overpotentials of different catalysts with current density of 10 mA cm^{-2}."

Comment 5 "*The intrinsic HOR activity (Figure 4c) should be normalized with the electrochemical active surface area (ECSA) which takes care of the loading and particle size effect. The ECSA determination should be done using Cu-stripping charge for the investigated system to see the real improvement in the performance for precise estimation (Neergat, M., V. Gunasekar, and R. K. Singh. "Oxygen Reduction Reaction and Peroxide Generation on Ir, Rh, and their Selenides–A Comparison with Pt and RuSe." Journal of the Electrochemical Society 158.9 (2011): B1060.).*"

Response: Thanks. To normalize with ECSA, we have performed the test using Cu underpotential deposition (Cu-UPD) cyclic voltammetry, and normalized the intrinsic HOR activity accordingly. As exhibited in Supplementary Fig. 28, the Cu-UPD tests demonstrate that the Co_s-SO-Ru exhibits a larger ECSA (152 m^2 g^{-1}) than that of Co_s-Ru (101 m^2 g^{-1}), which may be attributed to the ability of S=O bonds to suppress Ru cluster agglomeration during pyrolysis process. Moreover, the Co_s-SO-Ru catalyst shows the highest ECSA-normalized exchange current density ($j_{0,\ ECSA}$) at 0.18 mA cm^{-2}, outperforming Co_s-Ru (0.12 mA cm^{-2}), Pt/C (0.04 mA cm^{-2}), and Ru/C (0.05 mA cm^{-2}). This indicates the outstanding HOR catalytic activity of Co_s-SO-Ru. These updates have been incorporated into the revised manuscript and supplementary information:

Page 9, line199: "***The j_0 was further normalized by electrochemical active surface area (ECSA) obtained via Cu underpotential deposition (Cu-UPD) tests (Supplementary Fig. 28). The Co_s-SO-Ru shows the highest $j_{0,\ ECSA}$ (0.18 mA cm^{-2}), indicating the superior specific activity.***"

Supplementary Information, Page 30:



Supplementary Fig. 29 Calculation of ECSA via the Cu underpotential deposition (Cu-UPD) methods for a Pt/C, b Ru/C, c Co_s-SO-Ru, and d Co_s-Ru. e The summary of the ECSA value for different catalysts. f The calculated $j_{0,\ ECSA}$ of different catalysts.

To perform the ECSA measurements, the CV curves are conducted in 0.5 M H_2SO_4 electrolyte, both in the absence (black) and presence (red) of 5 mM $CuCl_2$. As exhibited in, the Co_s-SO-Ru exhibits a larger ECSA (152 $m^2\ g^{-1}$) than that of Co_s-Ru (101 $m^2\ g^{-1}$). Moreover, the Co_s-SO-Ru shows the highest ECSA normalized exchange current density ($j_{(0,\ ECSA)}$ at 0.18 mA cm^{-2}, outperforming Co_s-Ru (0.12 mA cm^{-2}), Pt/C (0.04 mA cm^{-2}), and Ru/C (0.05 mA cm^{-2}), indicating the superior HOR catalytic activity of Co_s-SO-Ru.

To obtain monolayered Cu atoms on metallic sites, the Pt/C and Ru-based electrodes were polarized at underpotentially deposited potentials for 100 s in 0.5 M H_2SO4 with 5 mM $CuCl_2$. The Cu-UPD stripping processes were conducted via oxidation of the monolayered Cu between 0.2-0.7 V. The ECSA was calculated via the integral areas of Cu-UPD peaks (Q_{Cu}) with the subtraction of the background. Using a charge density of 420 μC cm^{-2} (Q_s):

$$ECSA\left(m^2_{metal}/g\right) = Q_{Cu}/(M_{metal} * Q_s)$$

where the M_{metal} is the mass loading of metal on the working electrode.

Comment 6 "*The HOR mass-activity comparison with the literature should be compared to the*

synthesized materials in this investigation."

Response: Thanks. Accordingly, we calculated the mass normalized kinetic current density ($j_{k,m}$) of different catalysts and compared them with previously reported state-of-the-art Ru-based catalysts in 0.1 M KOH (**Supplementary Table 5**). The mass activity of Co_s-SO-Ru (3.44 A mg_{Ru}^{-1}) is 2.49 times higher than that of Co_s-Ru (1.38 A mg_{Ru}^{-1}) and it outperforms other reported noble-metal-based catalysts. This highlights the advantage of sulfo-oxygen bridged Co-Ru sites:

Page 9, Line 190-192: "The exchange current density (j_0) of different samples is obtained by the fitting of micro-polarization region. ***The Co_s-SO-Ru shows a higher j_0 (3.51 mA cm^{-2}) (Fig. 4c) and mass activity ($j_{k,m}$) (3.44 A mg_{metal}^{-1}) than those of Co_s-Ru and other state-of-the-art electrocatalysts (Supplementary Table 5, 6)***, thus evidencing the enhanced intrinsic activity."

Supplementary Information:

"***Supplementary Table 5. Comparison of mass-normalized HOR activities with various recently reported state-of-the-art noble-metal-based catalysts in 0.1 M KOH.***

Catalysts	Catalysts loading (μg cm^{-2})	$j_{k,m}$ (A mg_{metal}^{-1})	Reference
Co_s-SO-Ru	***14.5***	***3.44***	***This work***
Co_s-Ru	***17.5***	***1.48***	***This work***
$Mn_1Ox(OH)y$ @Ru/C	***230***	***0.29***	***Nat. Catal.*** 3, 454-462 (2020)
Ru-$Cr_1(OH)x$-1.1	***60***	***0.43***	***Nat. Commun.*** 13, 5894 (2022).
Ru/RuO_2-180	***20***	***0.92***	**Adv. Mater.** 2023, 35, 2208821.
Ru-Ru_2P/C	***8.33***	***1.26***	***Angew. Chem. Int. Ed.*** 2022, 63, 202215585
Ru/VOC	***18.47***	***3.44***	***J. Am. Chem. Soc.*** 2023, 145, 27867-27876
Ru-V2O3/OC	***22.5***	***1.02***	
$RuNi_1$	***8.8***	***2.7***	**Nano Lett.** 2020, 20, 3442-3448
Ru_2P/C	***6.45***	***0.877***	***Angew. Chem. Int. Ed***. 2024, 63, e202406888.
PtRu/Mo_2C–W_2C	***13***	***0.40***	**ACS Catal.** 11, 932-947 (2021)
RuP/NOC	***18.1***	***3.25***	**Adv. Mater. Interfaces** 2022, 9, 2102193.

O-Pt3In/rGO[a]	***10***	***2.306***	***J. Am. Chem. Soc.*** 2024, 146, 29, 20323–20332
Pt NCs[a]	***10***	***2.128***	***Nat. Commun.*** 2022, 13, 1596.
PtMo NPs/C[a]	******	***0.805***	***Adv. Mater. 2023,*** 35, e2211854
Co0.2Ru0.7Pt 0.1/PNC[a]	***15***	***1.84***	***Angew. Chem., Int. Ed.*** 2023, 62, e202306881.
La_1Pt@HCS[a]	***10***	***2.42***	***Nat. Commun.*** 2023, 14, 3767
PmPt@IrPd[a]	***9***	***1.05***	***J. Am. Chem. Soc.*** 2023, 145, 4088-4097.
HEA-PdNiRuIrRh[a]	***6.98***	***3.25***	***Angew. Chem. Int. Ed.*** 2023, 62, e202217976
Pt SACs/CrN[a]	***4.5***	***2.8***	***Adv. Mater.*** 2023, 35, 2208799
Ni-Ir(BSC)/G[a]	***31.8***	***0.33***	***J. Am. Chem. Soc.*** 2023 145 (25), 13805-13815

[a] Pt or Ir-based catalysts for alkaline HOR."

Comment 7 "*On page 9, lines 182-183, "According to the Koutecky-Levich equation, the slope for HOR at Cos-SO-Ru electrode determined is 4.51 cm^2 $mA^{-1}s^{-1}$, similar to the theoretical value...." There is no support for the theoretical value. The author should also include the electron transfer during the HOR.*"

Response:

Thank you for your insightful comments and helpful suggestions. The theoretical value (4.87 cm^2 mA^{-1} $s^{-1/2}$) for two-electron transfer process during HOR is provided and the number of transferred electrons is calculated on the basis of the Koutecky-Levich (K-L) equation,

$$B = \frac{1}{Slope} = 0.62\, nF\, C_0 (D_0)^{\frac{2}{3}} v^{-\frac{1}{6}}$$

where B is the Levich constant, n is the number of transferred electrons, F is the Faraday constant (96,485 C mol^{-1}), C_0 is the solubility of H_2 in electrolyte, D_0 is the diffusivity of H_2 in electrolyte, v is the kinematic viscosity of the electrolyte. The number of transferred electrons is calculated as 2.09, which is slightly higher than the two-electron process. The higher number of transferred electrons could be attributed to the slight oxidation of catalysts. The corresponding details can be found in the revised manuscript:

Page 9, Line 183-186:

"***According to the Koutecky-Levich equation, the slope for HOR at Co_s-SO-Ru electrode is***

determined as 4.51 $cm^2\ mA^{-1}s^{-1/2}$, which is similar to the theoretical value (4.87 $cm^2\ mA^{-1}s^{-1/2}$). The calculated number of transferred electrons is 2.09, with the extra transferred electrons possibly attributed to the slight oxidation of catalysts."

Page 18, Line 407: "***The kinetic current density (j_k) was obtained according to the Koutecky-Levich (K-L) equation,***

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} \qquad (1)$$

where the j, j_k, and j_d are the measured current density, kinetic current density, and diffusion-limit current density, respectively. The HOR is dominated by H_2 diffusion and transport process due to the limited solubility in electrolyte. Thus, the diffusion-limited current density follows the (K-L) equation as:

$$j_d = BC_0\omega^{\frac{1}{2}} = 0.62\,nFC_0(D_0)^{\frac{2}{3}}v^{-\frac{1}{6}} \qquad (2)$$

where B is the Levich constant, n is the number of transferred electrons, F is the Faraday constant (96,485 $C\ mol^{-1}$), C_0 is the solubility of H_2 in electrolyte, D_0 is the diffusivity of H_2 in electrolyte, v is the kinematic viscosity of the electrolyte."

Comment 8 "*The author should compare the HOR exchange current density with the literature results in Figure 4. For instance, how does it compare with the Ru-based catalyst reported in the literature? Chen, Luyun, et al. "Confining Flat Ru Islands into TiO_2 Lattice with the Coexisting Ru–O–Ti and Ru–Ti Bonds for Ultra-Stable Hydrogen Evolution at Amperometric Current Density and Hydrogen Oxidation at High Potential." Advanced Science: 2410881;*
Zhu, Y., Klingenhof, M., Gao, C. et al. Facilitating alkaline hydrogen evolution reaction on the hetero-interfaced Ru/RuO2 through Pt single atoms doping. Nat Commun 15, 1447 (2024) https://doi.org/10.1038/s41467-024-45654-9;
Zhou, Y., Xie, Z., Jiang, J. et al. Lattice-confined Ru clusters with high CO tolerance and activity for the hydrogen oxidation reaction. Nat Catal 3, 454–462 (2020). https://doi.org/10.1038/s41929-020-0446-9"

Response: Thanks. Accordingly, we have carefully re-calculated the HOR exchange current density (j_0) and mass normalized j_0 ($j_{0,m}$) of different catalysts. Our results demonstrate that the Co_s-SO-Ru exhibits a superior j_0 and $j_{0,m}$ compared with other state-of-the-art catalysts, indicating the high catalytic efficiency of the S=O bond-bridged Co-Ru sites. The corresponding details have been updated in the revised manuscript and supplementary information:

Page 9, Line 190-192: "***The Co_s-SO-Ru shows a higher j_0 (3.51 $mA\ cm^{-2}$) (Fig. 4c) and mass activity ($j_{k,m}$) (3.44 $A\ mg_{metal}^{-1}$) than those of Co_s-Ru and other state-of-the-art electrocatalysts***

(Supplementary Table 5, 6), thus evidencing the enhanced intrinsic activity."

Supplementary Information:

"**Supplementary Table 6.** ***Comparison of exchange current density and mass-normalized HOR activity with previously reported state-of-the-art noble-metal-based catalysts in 0.1 M KOH.***

Catalysts	Scan rate (mV s^{-1})	j_0 (mA cm^{-2})	Mass-normlized $j_{0,m}$ (mA mg^{-1})	Reference
Co_s-SO-Ru	***5***	***3.51***	***280***	***This work***
Co_s-Ru	***5***	***2.45***	***140***	***This work***
Pt_6NCs/C	***5[a]***	***3.23***	***/***	***Nat.Communun***. 13,1596(2022)
Ru colloidosomes	***5[a]***	***2.86***	***50.18***	***J. Am. Chem. Soc.*** 11138-11147 (2022)
Ru@TiO_2	***10***	***2.0***	***79.78***	***Nat. Catal.* 3, 454-462 (2020)**
Ni-H_2-NH_3	***8.33***	***~1.10***	***21.95***	***Nat. Mater. 21, 804-810 (2022)***
Ru_2P	***10***	***1.98***	***389***	***Angew. Chem. Int. Ed***. 2024, 63, e202406888.
RuP	***10***	***1.13***	***207***	
PdCu/C-500 °C	***1***	***1.63***	***127.62***	***J. Am. Chem. Soc.*** 140, 16580-16588 (2018)
$Ir_3Pd_1Ru_6$/C	***5***	***2.55***	***728.57***	***J. Am. Chem. Soc.*** *139, 6807-6810 (2017).*
RuP@RuP_2/C	***10[a]***	***2.65***	***49.26***	***Adv. Mater.*** 34, 2204624 (2022)
pc Pt with1-methylimidazole	***10***	***~1.30***	***/***	***Angew. Chem. Int. Ed.*** e202207197 (2022)

[a] **Conducted with a rotation speed of 2500 rpm. Other results are obtained with a rotation of speed of 1600 rpm.**

Comment 9 "*The CO-poisoning tests for HOR should highlight the robustness of the catalyst with CO tolerance in the hydrogen-fed anode for fuel cell applications.*"

Response: Thanks. According to your feedback, CO anti-poisoning test was performed in 0.1 M KOH

with a mixture of H_2 and CO (100 ppm). As exhibited in **Fig. R7**, the Co_s-SO-Ru shows less decay in HOR current density (16.7%) with presence of CO, whereas the Co_s-Ru suffers a more significant loss (48.0%) under the same conditions. These results demonstrate that atomically S=O bridges would efficiently prevent CO adsorption on Ru sites.

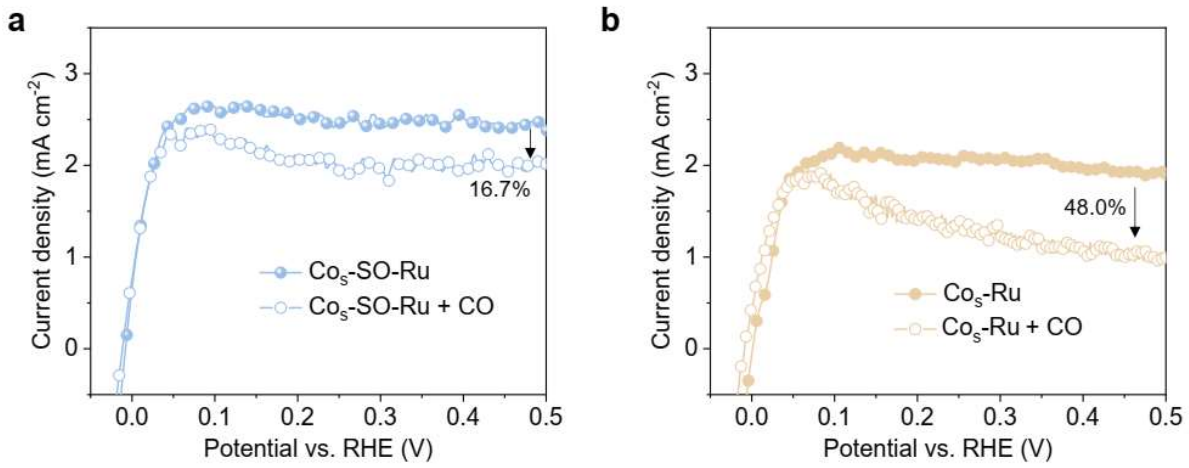


Fig. R7 a HOR polarization curves of Co_s-SO-Ru in 0.1 M KOH with or without 100 ppm CO. **b** HOR polarization curves of Co_s-Ru in 0.1 M KOH with or without 100 ppm CO.

Comment 10 "*The HOR polarization presented in Figure 4a can be extended to a higher potential of ~0.8 V vs. RHE.*"

Response: Thanks. We have conducted additional tests on the HOR polarization curves at higher oxidation potentials in H_2-staturated 1.0 M KOH with a hydrogen flow rate of 300 mL min^{-1}. As exhibited in Fig. 3a, the Ru/C presents a dramatic decrease in catalytic activity when the oxidation potential exceeds 0.4 V. This behavior is attributed to the high oxophilicity of Ru sites, which tends to be occupied by oxygen species (OH*). In contrast, the Co_s-SO-Ru exhibits only a slightly decrease in current density even at potentials above 0.8 V. The corresponding discussions have been added in the revised manuscript:

Page 8, line 181: "***As shown in Fig. 4a, the Co_s-SO-Ru exhibits the highest diffusion-limited current density (2.67 mA cm^{-2}) than those of Co_s-Ru (2.05 mA cm^{-2}), Ru/C (1.62 mA cm^{-2}), and Pt/C (1.86 mA cm^{-2}).***"

Page 9, line 186: "***Moreover, compared with Ru/C, the Co_s-SO-Ru exhibits stable current density at high oxidation potentials above 0.8 V,*** which would be contributed to the low oxophilicity of Ru sites and the oxide-free catalytic surface for Co_s-SO-Ru."

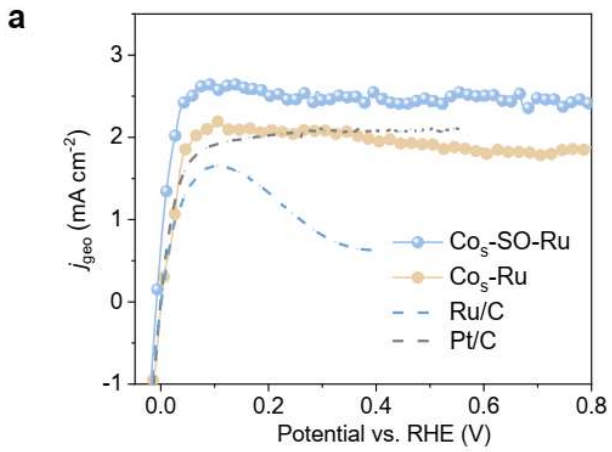


Fig. 4a HOR curves of different catalysts in H_2-saturated 0.1 M KOH with hydrogen flow rate of 300 mL min^{-1}.

Comment 11 "*The focus of the paper is on alkaline HOR. Why anion-exchange membrane fuel cell test was not performed? The authors should justify their take on this. A few sentences should be included on the AEMFC in the introduction to improve the broadness of the article*."

Response:

Thanks for your important and helpful comments on improving the quality of our manuscript. Owing to the outstanding HOR performance of Co_s-SO-Ru, we then made it as the anode catalyst for hydroxide exchange membrane fuel cell (HEMFC). As exhibited in Fig.4e, the Co_s-SO-Ru presents a peak power density of 1.02 W cm^{-2} at 2.96 A cm^{-2}, outperforming the Pt/C anode with power density of 0.75 W cm^{-2} at 1.84 A cm^{-2}. Besides, the Co_s-SO-Ru also display superior stability with operation voltage increase of 0.1 V after 40 h operation, demonstrating the great potential for practiacl applications.

To improve the broadness of this work, we have stressed the importance of HEMFC in hydrogen economics. The corresponding results and discussions are provided in the manuscript and supplementary information:

Page 3, line 48: "***The sustainable hydrogen cycle has been considered as a viable strategy to reduce the consume of fossil fuels[1, 2]. Compared with proton exchange membrane fuel cells, hydroxide exchange membrane fuel cell (HEMFC) and water electrolysis (HEMWE) technologies are attractive for renewable hydrogen economy[3-5], which allow for exploring cost-effective non-platinum catalysts for efficient hydrogen evolution and oxidation reactions (HER and HOR)[6-8]***."

Page 10, line 216: "***Encouraged by the remarkable HOR catalytic performance of Co_s-SO-Ru, the***

membrane electrode assembly was fabricated using Co_s-SO-Ru or Pt/C (0.1 mg_{Ru} cm^{-2}) as the anode and Pt/C (0.4 mg_{Pt} cm^{-2}) as the cathode. Fig. 4e illustrates that the Co_s-SO-Ru achieves a peak power density of 1.02 W cm^{-2} at a current density of 2.96 A cm^{-2}, surpassing the performance of the Pt/C anode, which exhibits a power density of 0.75 W cm^{-2} at 1.84 A cm^{-2}. Additionally, the Co_s-SO-Ru display superior stability with a 0.1 V voltage increase after 40 h of operation (Supplementary Figure 34), demonstrating the great potential for practiacl applications.

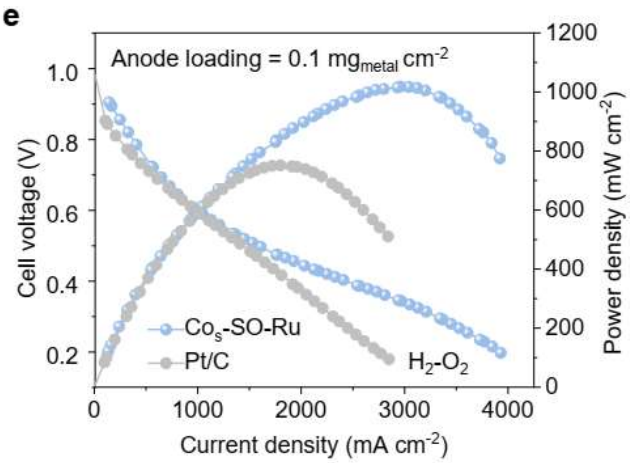
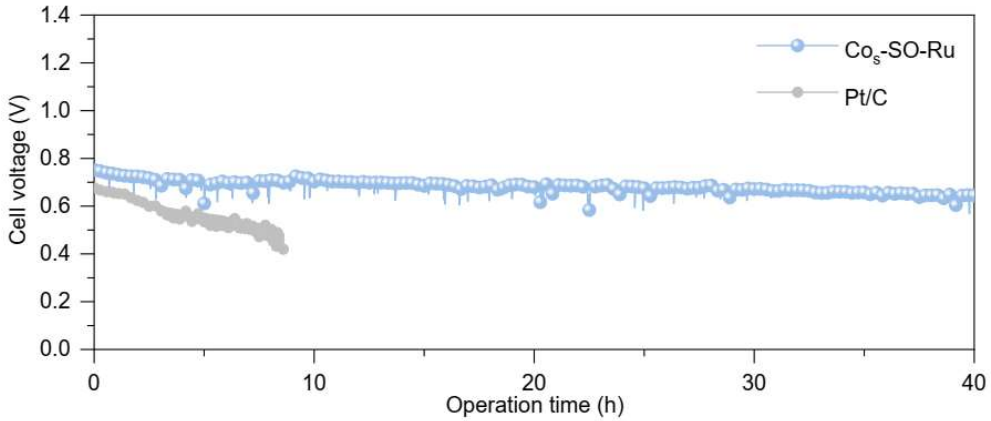


Fig. 4e Polarization and power density curves of HEMFCs using different catalysts as anode. Test conditions: Using Co_s-SO-Ru or Pt/C (0.1 mg_{Ru} cm^{-2}) as anode and Pt/C (0.4 mg_{Pt} cm^{-2}) as cathode with H_2 and O_2 flow rate of 1.0 L min^{-1}. The cell, anode, and cathode humidifier temperatures are 80, 77, and 79 °C, respectively; back pressures were symmetric at 200 kPag for both sides.

Supplementary Information, Page 36:



Supplementary Figure 34. The long-term durability test for HEMFCs using Co_s-SO-Ru or Pt/C as anode with current density of 500 mA cm^{-2}."

Comment 12 "*In Figure 4i, the HER performance of the Pt looks very low. Authors are advised to check the literature data to justify this*."

Response: We sincerely appreciate your valuable comments and constructive feedback, which have played an essential role in improving our manuscript. We acknowledge your point that the Pt/C show poor HER performance. To address this, we have re-tested the HER catalytic performance of Pt/C in 1.0 M KOH with real-time iR correction, which will help to better compare the HER catalytic activity of different catalysts, as shown as below:

Manuscript, Page 11, Line 228-229: "

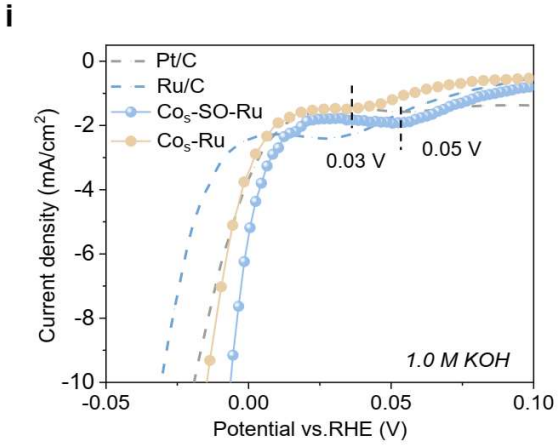
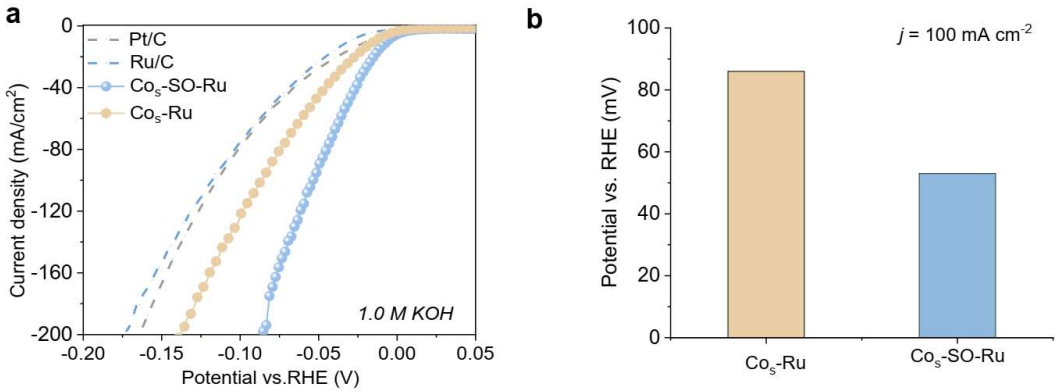


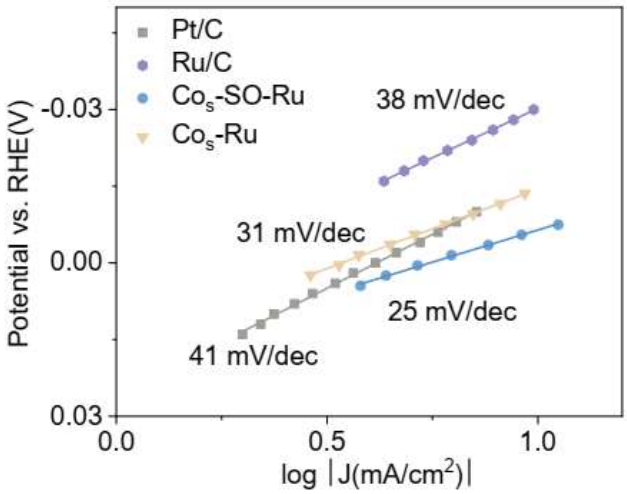
Fig. 4i HER curves of different catalysts in 1.0 M KOH with real-time iR correction.

Supplementary Information, Page 31:



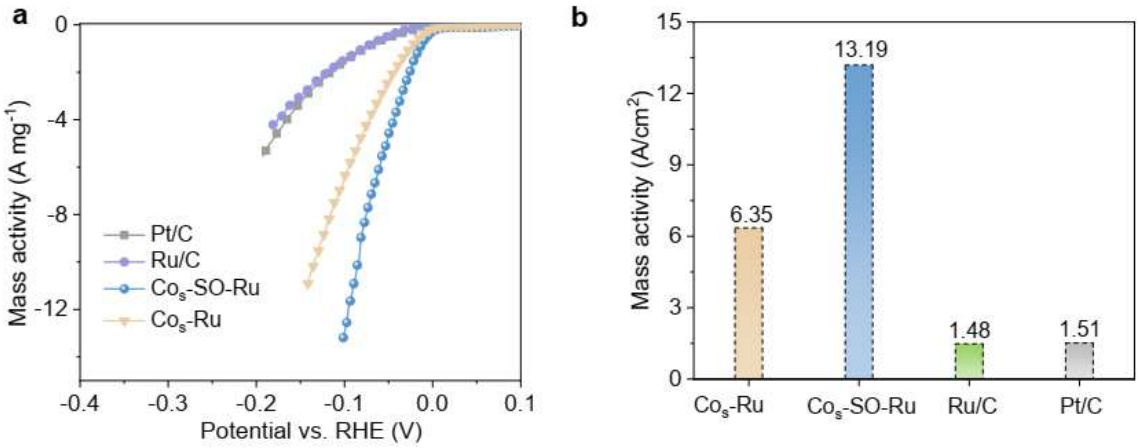
Supplementary Figure 36. a Comparison of HER polarization curves of different catalysts in 1.0 M KOH. b The overpotentials of different catalysts with current density of 100 mA cm^{-2}.

Supplementary Information, Page 32:



Supplementary Figure 38. The Tafel slope of different samples.

Supplementary Information, Page 33:



Supplementary Figure 39. a The mass activity of different catalysts in alkaline conditions that normalized by the noble metal mass. b The mass activity of different catalysts obtained with potential of -0.1 V.

Point-by-point response to the detailed comments by the reviewers of *"Sulfo-oxygen bridges optimize interfacial water for alkaline hydrogen oxidation/evolution reactions"* with manuscript ID: NCOMMS-24-56191A

Reviewer #1

Comment 1: *Although the author has explained the novelty issue and improved the data quality, there are still some serious problems, as follows. The synchrotron radiation absorption spectrum is essential data for verifying the structure. Although the data shows that there is no Co-Co bond length in the sample, this is in line with the author's expectations. However, we found serious issues with the data of the standard sample Co-Foil. As a conventional sample, the Co-Co bond length of Co-Foil is much smaller than the normal value (around 2.5 Å). This is very strange, so we reasonably doubt the authenticity of the author's data.*"

Response: Thank you for your insightful question. The Co foil shows an intensive peak at around 2.18 Å in R-space (**Fig. 3g**). The peak position is consistent with that of the standard Co foil (*Nat Catal* **7**, 702–718 (2024); *J. Am. Chem. Soc.* 2023, 145, 17329-17336). Although the value is related to Co-Co bonds, the observed peak position cannot be directly equated to the actual Co-Co bond length. Instead, the bond length is derived through EXAFS fitting analysis, which yields a refined bond length of 2.49 ± 0.02 Å (Table S4). This value aligns well with conventional reference data (around 2.5 Å), as noted by the referee.

Notably, the observed shift of peak position in in R-space would be attributed to the scattering phase-shift according to the EXAFS equation (Rev. Mineral. Geochem. 78, 33-74 (2014)):

$$\chi(k) = \sum \frac{Nf(k)e^{-2k^2\sigma^2}}{kR^2} \sin[2kR + \delta(k)]$$

where *f(k)* is the scattering amplitude and *δ(k)* is phase-shifts. *N* is the number of neighboring atoms, *R* is the distance to the neighboring atom, and σ^2 is the disorder in the neighbor distance. In Athena software, the default data processing model does not apply phase correction, leading to an apparent peak shift of approximately -0.5 Å. Consequently, the observed peak positions in R-space appear shorter than the actual atomic distances. To address this issue, we reprocessed the Co foil data using Athena with the phase correction option enabled. As shown in Fig. R1, after applying phase correction, the main peak corresponding to the Co-Co bond in R-space shifts to ~2.47 Å which is in good agreement with our EXAFS fitting results. We appreciate your valuable feedback and hope this clarification resolves your concerns.

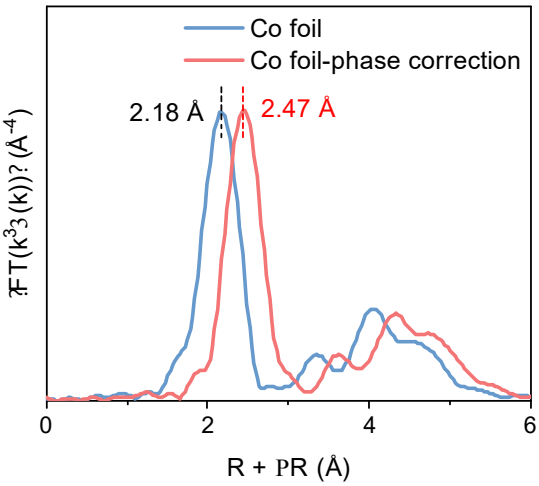


Fig. R1. EXAFS curves in R-space for Co foil with and without phase correction.

Comment 2: "*Regarding our question that the data provided in the HAADF-STEM graph does not fully support the existence of single atoms on carbon carriers, the response that the author's intention never claimed the existence of single atom positions on carbon substrates is not valid. Because some of the author's data, such as synchrotron radiation absorption spectra, clearly show the absence of Co-Co bond lengths in the sample, and the author's response also states that "the author believes that atomic dispersed Co sites cannot be directly observed in HAADF-STEM images due to the weaker signal intensity of Co species compared to Ru species". All of these indicate that the author himself agrees with the viewpoint of Co atom dispersion. The author believes that "the inability to observe atomically dispersed Co sites in HAADF-STEM images directly is due to the weaker signal intensity of Co species compared to Ru species" cannot be used as a reason for the insufficient quality of HAADF-STEM data, as in the reference "Single-atom Mo tail high-entropy all ultrathin nanosheets with intrinsic tensile strain enhancement electrocatalysis, Nature Communications, 2024." Mo species have weaker signal intensity than Pt species but can still be well displayed. Therefore, the author is responsible for improving the quality of HAADF-STEM to verify this. In addition, we have found that the resolution of HAADF-STEM is not high enough. Please improve the quality. Please provide the high-resolution mapping of aberration-corrected electron microscopy, which will more clearly display the structural information of the sample, which is very important*."

Response: We sincerely appreciate the reviewer's valuable suggestions. In response to your concerns, we have improved the quality of the HAADF-STEM images and provided high-resolution aberration-corrected electron microscopy mapping (**Fig. 2f, Supplementary Figs. 10 & 11**). As shown in the revised manuscript, the high-resolution EDX element mapping demonstrates that the Co signal is

sporadically distributed on the Ru clusters. This preliminary evidence supports the atomic dispersion of Co sites in Co_s-SO-Ru. Furthermore, XAS results (**Fig. 3g**) confirm the absence of Co-Co bonds. Therefore, the Co single atoms are likely distributed on Ru clusters through the easy formation of metal-sulfur bridge bonds. To enhance structural visualization, we have included high-resolution aberration-corrected STEM images in the revised manuscript and supporting information. The corresponding discussion has also been updated accordingly:

Page 5, line 116: **"Instead, the high-resolution HAADF-STEM images demonstrate that the atomic cobalt preferentially disperses on Ru nanoclusters through the easy formation of metal-sulfur bridge bonds (Fig. 2d)[45]. The signal intensity profiles obtained from HAADF-STEM image demonstrate the periodic arrangements of Ru sites (Fig. 2e)[46, 47]. Additionally, high-resolution energy dispersive X-ray spectroscopy (EDX) elemental mappings demonstrate that the Co signal is sporadically distributed across the Ru clusters, providing preliminary evidence for the atomic dispersion of Co sites in Co_s-SO-Ru (Fig. 2f, Supplementary Figs. 10,11)."**

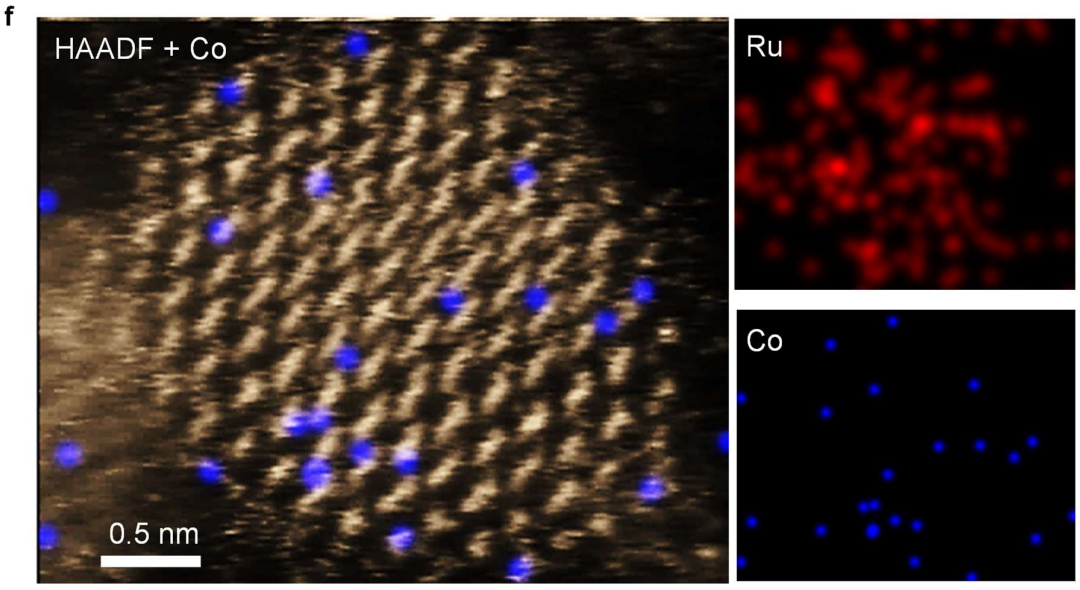
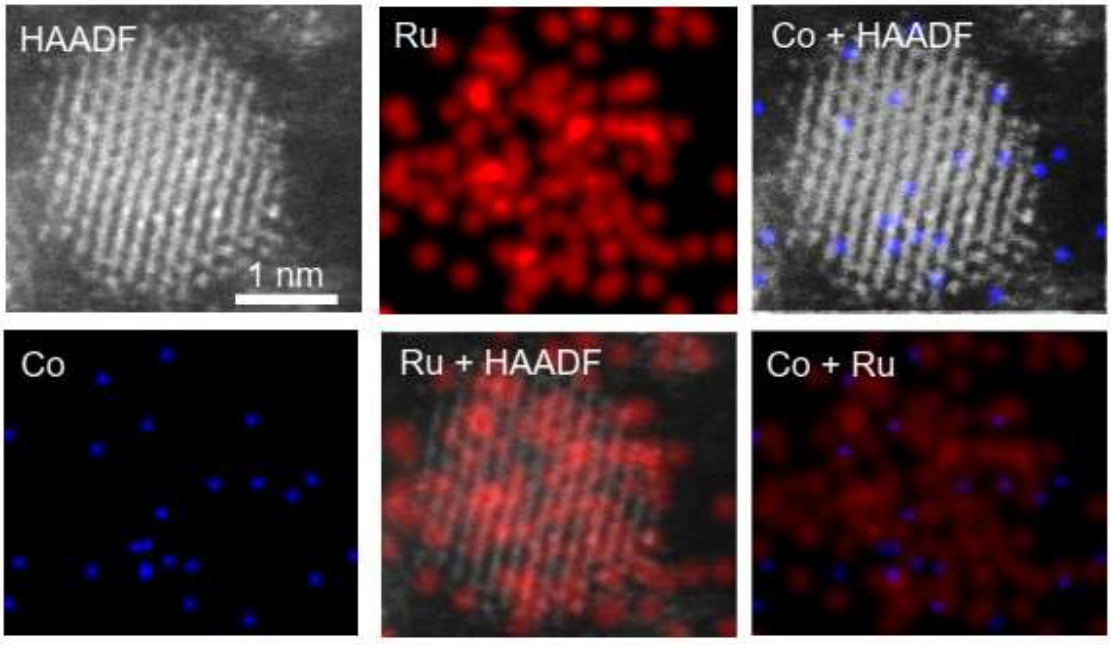
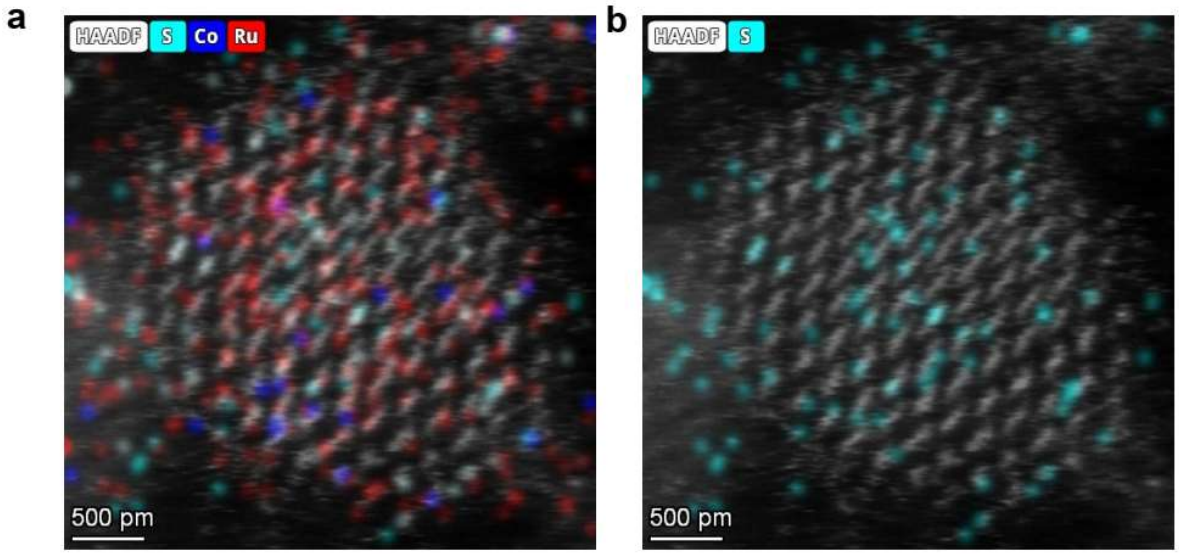


Fig.2f Atomic-resolution HAADF-STEM image of Co_s-SO-Ru and the corresponding EDX mapping results of Ru and Co elements.



Supplementary Figure 10. HAADF-STEM images of Co_s-SO-Ru and corresponding EDX mappings.



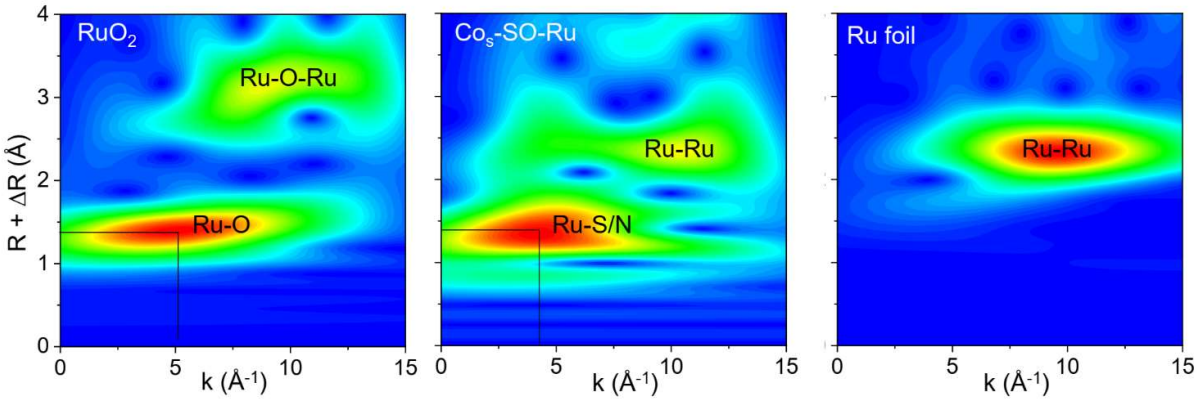
Supplementary Figure 11. HAADF-STEM image of Co_s-SO-Ru and corresponding EDX mappings.

Comment 3: "*The wavelet transform of the synchrotron radiation absorption spectrum can clearly show the coordination of metals. Please supplement this data.*"

Response: We sincerely appreciate the reviewer's valuable suggestion. The wavelet-transforms (WT) of k^3-weighted extended X-ray absorption fine structure (EXAFS) spectrum have been provided in

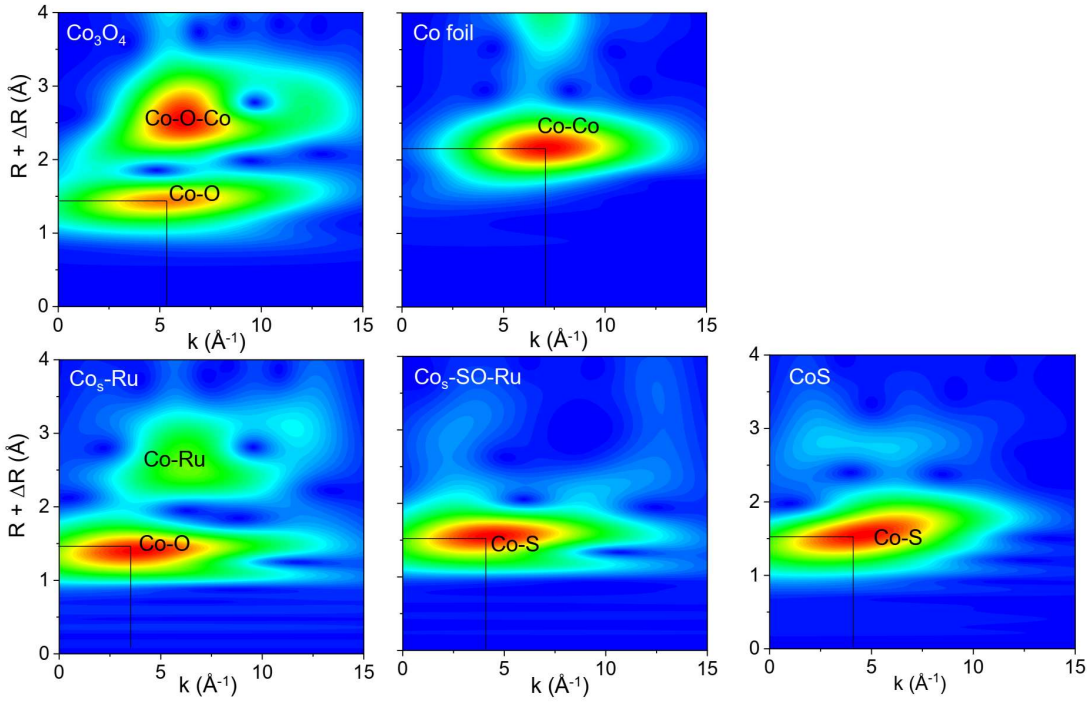
Supplementary Information to illustrate the metal coordination environment. The WT-EXAFS images for Co_s-SO-Ru exhibit a slightly longer Ru-S/N peak compared to Ru-O peak, indicating the mixture coordination of Ru-S/N with the relatively long Ru-S bonds (**Supplementary Figure 20**). Importantly, WT images at the Co *K*-edge show the predominant Co-S bonds (2.23 Å) in the first coordination shell, similar with those in CoS (**Supplementary Figure 22**). The finding confirms the formation of sulfo-oxygen bridged Co single-atoms. Additionally, the Co_s-Ru exhibits a longer Co-Ru bond than that of Co-Co bond in Co foil. Thus, the Co single-atoms would be doped in Ru clusters. The corresponding results and discussions are provided in Supplementary Information, as outlined below:

Supplementary Information:



Supplementary Figure 20. WT-EXAFS for Ru foil, Co_s-SO-Ru, and RuO_2.

WT-EXAFS images for Co_s-SO-Ru exhibit slightly longer Ru-S/N peak than Ru-O peak, indicating the mixture coordination of Ru-S/N with the relatively long Ru-S bonds.



Supplementary Figure 22. WT-EXAFS for Co foil, Co_3O_4, Co_s-Ru, and Co_s-SO-Ru.

Importantly, WT images at the Co *K*-edge show the predominant Co-S bonds (2.23 Å) in the first coordination shell similar with that of CoS, demonstrating the formation of sulfo-oxygen bonds bridged Co single-atoms. Besides, the Co_s-Ru exhibits a longer Co-Ru bond than that of Co-Co bond in Co foil, confirming that the Co single-atoms are doped onto the surface of Ru clusters.

Comment 4: "*Please improve the data quality of Figure 2g*."

Response: We sincerely appreciate the reviewer's valuable suggestion. In response, the quality of Fig.2g have been improved based on the high-resolution HAADF-STEM images. The updated figure is shown below:

Page 5, line 22: **"The signal intensity profiles obtained from HAADF-STEM image demonstrate the periodic arrangements of Ru sites (Fig. 2e)."**

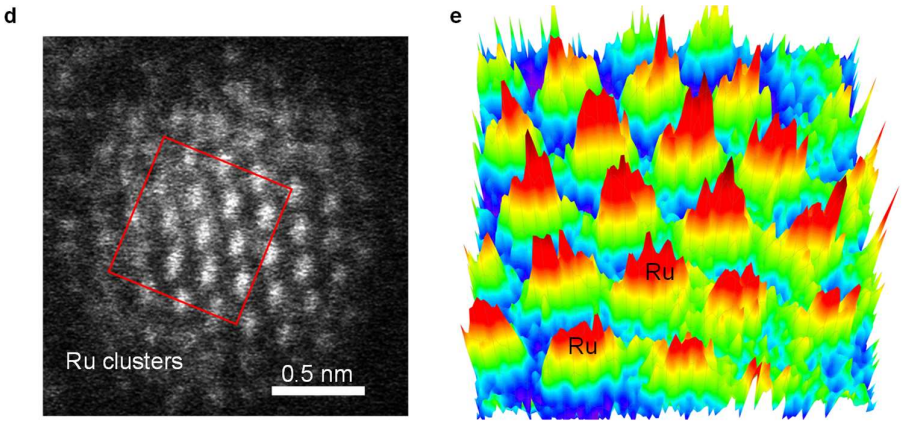


Fig.2d Atomic-resolution HAADF-STEM images of Co_s-SO-Ru and **e** corresponding plane intensity profiles labeled with red boxes in **d**.

Comment 5: "*Please enhance the aesthetic level of Figure 5f.*"

Response: Thanks. Fig.5f has been carefully revised.

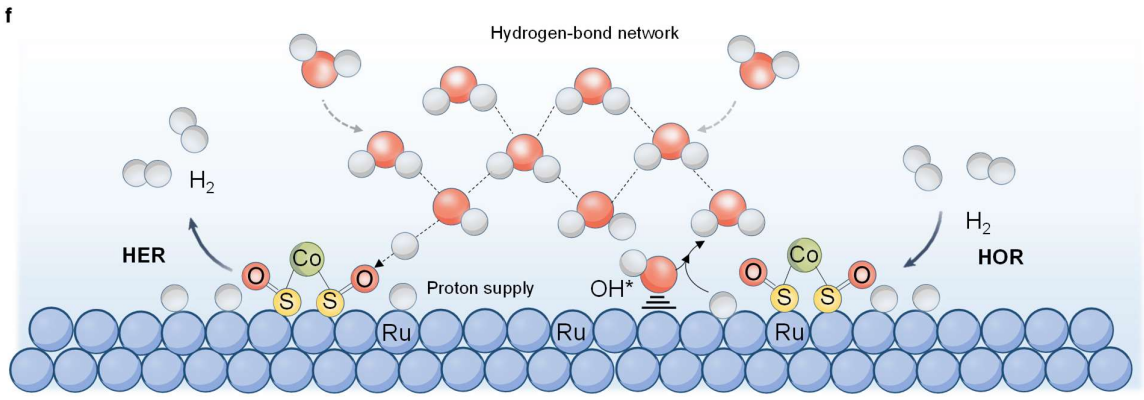


Fig. 5f The schematic illustration of the dynamic hydrogen-bond network conformations.

Reviewer #3 :

The authors have addressed most of my concerns, and it can be accepted now.

Response: We sincerely appreciate your kind support and valuable feedback.

Reviewer #4: "*The authors answered satisfactorily the comments raised by doing the additional experiments. Therefore, I accept the manuscript after answering minor comments:*"

Response: We sincerely appreciate your kind support and valuable feedback. In response to the insightful comments, as well as those from other reviewers, we have conducted additional experiments and refined the manuscript accordingly.

Comment 1: "*In the introduction Page 3, lines 48-51 "The sustainable hydrogen cycle has been considered as a viable strategy to reduce the consume of fossil fuels1,2. Compared with proton exchange membrane fuel cells, hydroxide exchange membrane fuel cell (AEMFC) and water electrolysis (AEMWE) technologies are attractive for renewable hydrogen economy3-5, which allow for exploring cost-effective nonplatinum catalysts for efficient hydrogen evolution and oxidation reactions (HER and HOR)6-8" Only reference 5 deals with AEMFC, please include the AEMWE and AEMWE papers and cite close to AEMFC or AEMWE for clarity. For instance, "AEMFC (Refs..xx) and AEMWE (Refs. yy...) and follow the same throughout the manuscript*."

Response: Thank you for your suggestion. To enhance clarity and accuracy, we have incorporated the appropriate references, Nat. Energy 9, 1297–1309 (2024) for AEMFC and Adv. Mater. 36, 2402184 (2024); J. Am. Chem. Soc. 2025, 147 (9), 7711–7720 for AEMWE, ensuring precise citation placement.

Page 3, line 48: "**Compared with proton-exchange-membrane fuel cells, anion-exchange-membrane fuel cell (AEMFC)[3] and anion-exchange-membrane water electrolysis (AEMWE)[4, 5] technologies are attractive for renewable hydrogen economy[6-8], enabling the exploration of cost-effective non-platinum catalysts for efficient hydrogen evolution and oxidation reactions (HER and HOR)[9-11]**."

Comment 2: "*Figure 4c, the j_0 values must be normalized with ESCA. Now it is not clear how it was normalized. Follow the J_0 values shown in SI Figure 29*."

Response: Thanks. To ensure a more accurate comparison of the catalytic activity of Co_s-SO-Ru with other reported catalysts, the j_0 values have been calculated by fitting micro-polarization region. Then, we carefully normalized j_0 using the electrochemical active surface area (ECSA), which was obtained via Cu underpotential deposition (Cu-UPD) tests (Supplementary Fig. 28). The Co_s-SO-Ru shows the highest $j_{0,\,ECSA}$ (0.45 mA cm^{-2}), confirming the superior specific activity. The ECSA normalized $j_{0,\,ECSA}$ have also been compared with previously reported state-of-the-art catalysts, as shown in Fig. 4c and Supplementary Table 7.

Page 9, line 200: "The j_0 values were further normalized by electrochemical active surface area (ECSA)

obtained via Cu underpotential deposition (Cu-UPD) tests (Supplementary Fig. 28). **The Co_s-SO-Ru catalyst shows the highest $j_{0,\,ECSA}$ (0.45 mA cm_{metal}^{-2}), indicating the superior specific activity compared to previously reported catalysts (Fig. 4c, Supplementary Table 7).**

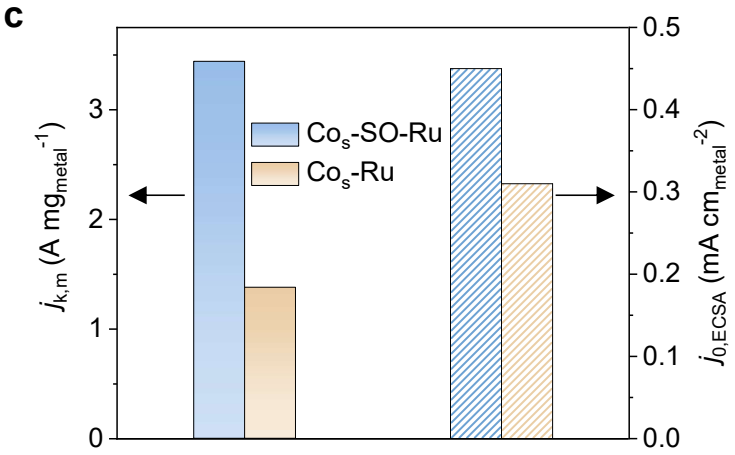
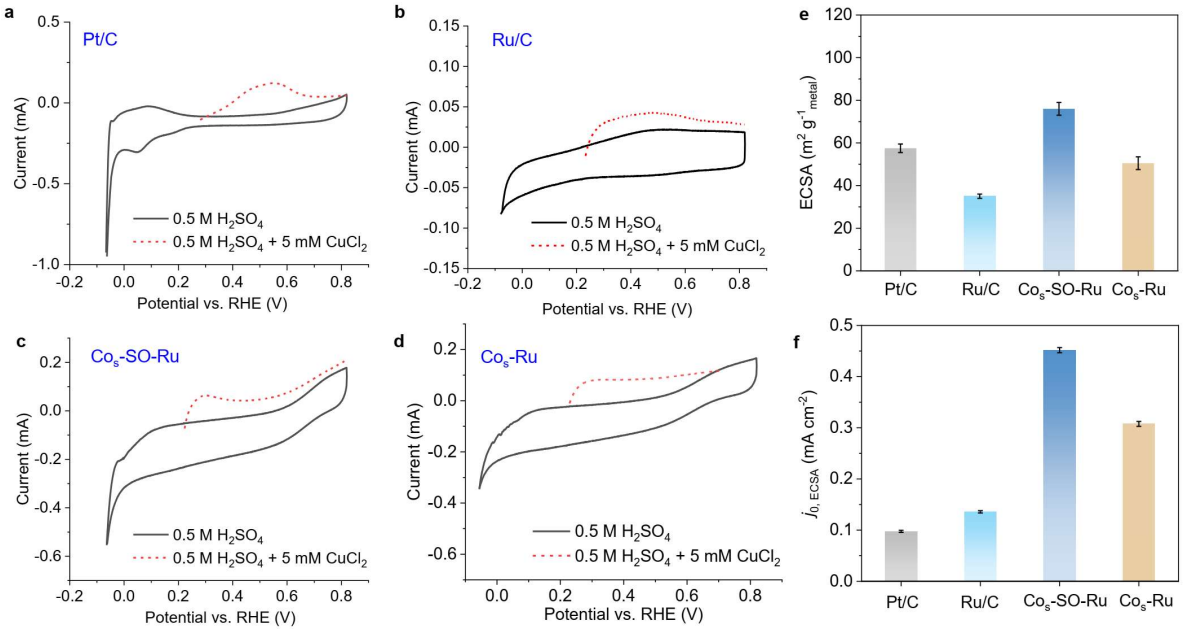


Fig. 4c Comparison of kinetic mass activity ($j_{k,m}$) with an overpotential of 50 mV and exchange current density ($j_{0,\,ECSA}$) normalized by ECSA.



Supplementary Fig. 28 Calculation of ECSA via the Cu underpotential deposition (Cu-UPD) methods for **a** Pt/C, **b** Ru/C, **c** Co_s-SO-Ru, and **d** Co_s-Ru. **e** The summary of the ECSA value for different catalysts. **f** The calculated $j_{0,\,ECSA}$ of different catalysts that normalized by ECSA.

Supplementary Table 7. Comparison of ECSA-normalized HOR activity with previously

reported state-of-the-art noble-metal-based catalysts in 0.1 M KOH.

Catalysts	ECSA-normlized $j_{0,ECSA}$ (mA cm_{metal}^{-2})	Reference
Co_s-SO-Ru	0.45	***This work***
Co_s-Ru	0.31	***This work***
$Mn_1O_x(OH)_y$@Ru/C	0.177	***J. Am. Chem. Soc.*** 2024 146 (24), 16619-16629
Pt/C	0.216	
Ru-CrO_x@CN	1.04	***Nat. Catal.*** 7, 441–451 (2024).
Ru@CN	0.95	
Ru-Cr_1(OH)x-2.2	0.28	***Nat. Commun.*** 2022, 13, 5894.
Ru_2P/C	0.389	***Angew. Chem. Int. Ed.*** 2024, 63, e202406888.
Rh_2Sb NBs	0.506	**Adv. Mater.** 2021, 33, e2105049.
Ir@Pd	0.294	***Adv. Mater.*** 2021, 33, 2105400.
di-RuNi MLNS/C	0.367	**Adv. Funct. Mater.** 2023, 33, 2210328.
HEA/C	1.19	***Angew. Chem. Int. Ed***. 2023, 62, e202217976.
PtRuNiCoFeMo HEA SNWs	0.969	**Nat. Commun.** 2021, 12, 6261.

Comment 3: "*In Supplementary Table 6, it is unclear how j_0 was compared, it must be compared to mA cm^{-2} ECSA. Authors are advised to revise accordingly. The Supplementary Tables 5 and 6 can be combined into one.*"

Response: We sincerely appreciate the reviewer's helpful comments. The j_0 values were first calculated by fitting the micro-polarization region, and then they were normalized by ECSA. The ECSA normalized $j_{0,\ ECSA}$ values have been compared with previously reported state-of-the-art catalysts, as shown in **Supplementary Table 7**. Regarding the suggestion to combine Supplementary Tables 5 and 6, we would like to clarify that the references summarized in these tables are distinct in nature, which makes it challenging to combine them into a single table. We hope the reviewer understands this distinction.

The revised Supplementary Table 7 now includes the $j_{0,\ ECSA}$ values normalized by ECSA for clarity and consistency.

Comment 4: "*On Page 9, The quoted text needs to be revised "The Co_s-SO-Ru shows a higher j_0 (3.51 mA cm^{-2}) (Fig. 4c) and normalized mass activity ($j_{k,m}$) (3.44 A $mgmetal^{-1}$) than those of Cos-Ru and other state-of-the-art electrocatalysts (Supplementary Table 5, 6)" J_0 should be compared to ECSA which is not the case here. The English must be polished throughout the manuscript e.g., "Supplementary Table 5, 6)" should be written as "(Supplementary Tables 5, 6)".*"

Response: We sincerely appreciate the reviewer's thoughtful comments. In response to your suggestion, we have revised the text as follows to ensure clarity and accuracy. Furthermore, the j_0 values were first calculated by fitting the micro-polarization region and then normalized by ECSA. The ECSA-normalized $j_{0,ECSA}$ values have been compared with previously reported state-of-the-art catalysts, as shown in Supplementary Table 7. Additionally, we apologize for the previous errors in the manuscript. We have carefully polished the text throughout to improve both clarity and language, including correcting the formatting of "Supplementary Tables 5 and 6" as requested.

Page 9, line 198: "The Co_s-SO-Ru shows a higher j_0 (3.51 mA cm^{-2}) (Fig. 4c) and normalized mass activity ($j_{k,m}$) (3.44 A mg_{metal}^{-1}) than those of Co_s-Ru and other state-of-the-art electrocatalysts **(Supplementary Tables 5, 6)**"

Page 9, line 209: "The TEM and HAADF-STEM images revealed that the spent catalyst retains similar structures and nearly unchanged size of Ru clusters (~ 1 nm) compared with the pristine Co_s-SO-Ru **(Supplementary Figs. 30,32)**"

Comment 5: "*The line numbers and the Figure numbers in the rebuttal is different from the article. Unify them for clarity*."

Response: We sincerely appreciate the reviewer's careful attention to detail. We have thoroughly checked and revised the figure numbers and line numbers to ensure consistency between the rebuttal, main manuscript, and supplementary information.

Comment 6: "*Why CoNi-SO/C is not active towards HOR? The author is advised to give more insight on this to solidify the impact.*"

Response: Thanks for the insightful comment. The poor HOR activity of CoNi-SO/C (**Fig. R2**) can be attributed to the following factors: (1) Tailoring the electronic structures of electrocatalysts to achieve an optimal hydroxide binding energy (OHBE) is crucial for the alkaline HOR. However, the

low oxyphilic Ni species would result in suboptimal adsorption behaviors of OH* intermediate, thereby suppressing HOR catalytic activity. (2) While Ni-based materials have been explored for HER/HOR, their catalytic performance remains inferior to PGM catalysts due to inherent electronic structure constraints. (3) During pyrolysis, Ni and Co tend to form bulk NiCo alloys (**Fig. R3**), which restricts the exposure of active sites. In contrast, Co_s-SO-Ru features small Ru clusters (~2 nm) dispersed on porous carbon, ensuring better catalytic accessibility. (4) The SO_4^{2-} counterions in CoNi-SO/C preferentially induce the formation of CoNi-based sulfide rather than sulfur-oxygen bonds. This prevents the establishment of interfacial hydrogen-bond networks critical for HOR. Additionally, the coexistence of CoNi alloys, Co_9S_8, and Ni_3S_2 in CoNi-SO/C (Figure R3) further disrupts active site uniformity, leading to poor HOR activity.

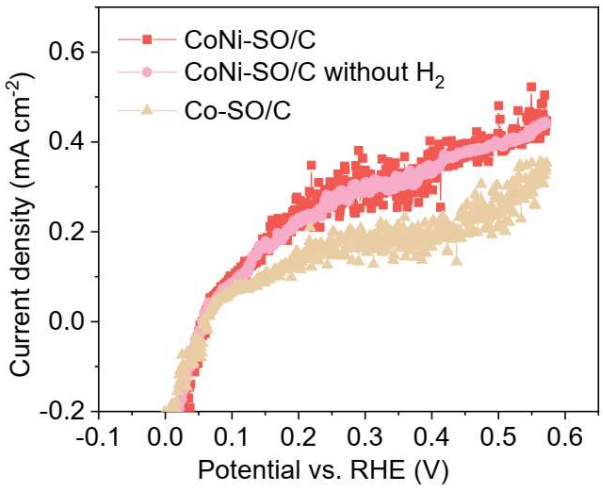


Fig. R2 The HOR polarization curves of Co-SO/C and CoNi-SO/C.

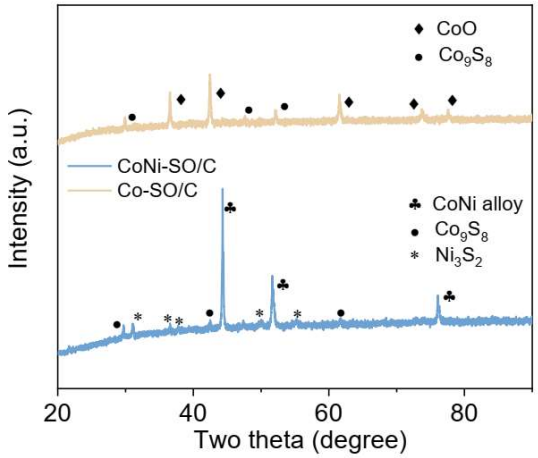


Fig. R3 The XRD patterns of CoNi-SO/C and Co-SO/C.

Point-by-point response to the detailed comments by the reviewers of *"Sulfo-oxygen bridges optimize interfacial water for alkaline hydrogen oxidation/evolution reactions"* with manuscript ID: NCOMMS-24-56191B

Reviewer #1: "*Regarding the issues with the article "Sulfo oxygen bridges optimize interfacial water for hydrogen electrocatalysis", although the author has provided some explanations, we still feel that there are some unreasonable aspects. We hope that the author can further explain and correct the following issues.*"

Response: We sincerely appreciate your kind support and valuable feedback. In response to your insightful comments, we have conducted additional explanations and refined the manuscript accordingly.

Comment 1: "*Regarding the bond length of the absorption spectrum, I previously pointed out that there were issues with the data processing of the bond length of the Co-Coil standard sample (Figure 3). Although the author explained that the reason for the bond length in the figure being 2.18 Å instead of the actual 2.47 Å was due to the lack of "Phase Correction". Firstly, performing "Phase Correction" is a necessary operation for absorption spectrum processing. Most literature will perform "Phase Correction" processing to obtain the actual bond length, as this is the real data we need. In this response, the author found that the actual bond length of Co-Coil was 2.47 Å after reprocessing it with "Phase Correction". So, what about the other data? Did they also be plotted without undergoing "Phase Correction" processing? For readers, this is a behavior that can easily cause misunderstandings and may even involve academic misconduct, so it is very necessary for us to conduct a detailed examination of this data. Please provide the results of each absorption spectrum with and without "Phase Correction". And please note in the caption of the main text whether the data has undergone "Phase Correction" to avoid any misunderstandings*."

Response: Thank you for this insightful and important comment. To enhance transparency and avoid any potential misunderstanding, we have now revised the coordinate of x-axis as *R(Å)* and clarified in figure captions that phase correction was not applied, in accordance with your suggestion.

To visually illustrate the phase shift between the peak positions (radial distances) and the actual bond lengths, we previously applied "phase correction" solely for explanation purposes in response to earlier reviewer comments. We would like to emphasize that bond lengths reported in the manuscript were determined through EXAFS fitting analysis, as presented in Supplementary Tables 3 and 4, and remain

unchanged from the original submission. It is important to note that bond lengths cannot be directly read from the radial distances in the EXAFS spectra. In other words, the "phase correction" was introduced only to help clarify the discrepancy between the peak positions in the Fourier-transformed (FT) EXAFS spectrum and the bond lengths derived from fitting. The peak positions in FT-EXAFS correspond to radial distances, not the true bond lengths which should be obtained via proper fitting. To avoid any confusion, we stress that phase correction is a separate operation and should not be equated with EXAFS curve fitting. For clarity, a response video was recorded to demonstrate the phase correction process, which was applied solely for illustrative purposes to demonstrate the phase shift in the radial distance.

As commonly acknowledged in the literature (e.g., *Chem. Soc. Rev.*, 2024, 53, 11850; *Rev. Mineral. Geochem.*, 2014, 78(1), 33–74), "phase correction" is not typically applied to standard FT or wavelet-transformed (WT) EXAFS spectra. We also provide an additional example in Figure R4, showing the EXAFS spectra without phase correction reported in previous studies (e.g., Nature 622, 754–760 (2023); Science 387, 48–55 (2025); Nat. Catal. 7, 702–718 (2024)). Therefore, the use of non-phase-corrected EXAFS spectra and the determination of bond lengths through fitting are widely accepted practices in the field. As such, this approach is unlikely to lead to misunderstandings among readers. We hope this addresses your concerns and provides sufficient clarification.

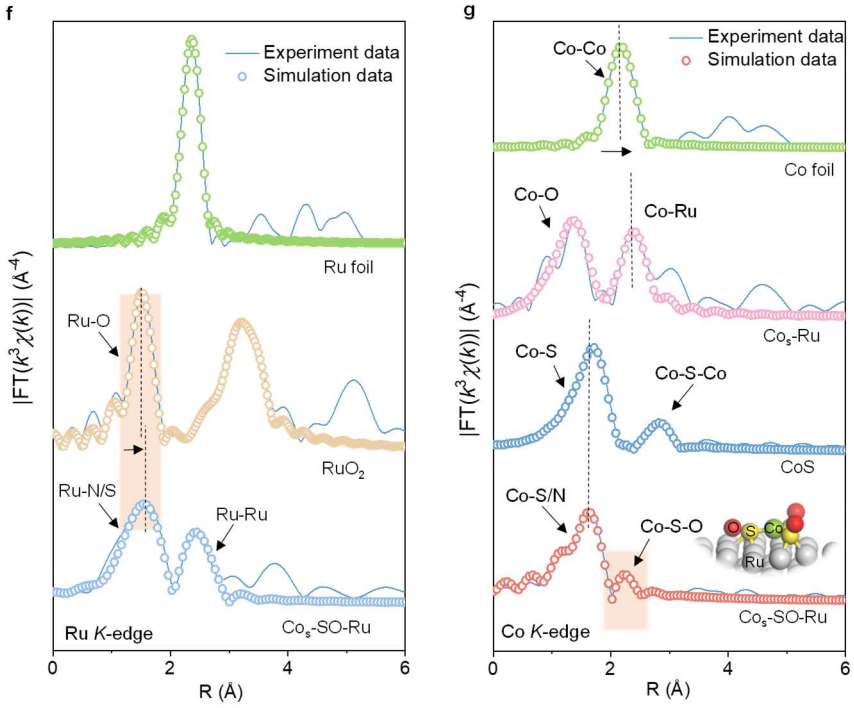


Fig. 3 FT-EXAFS in R-space and corresponding fitting curves for **f** Ru foil, RuO_2, Co_s-SO-Ru and **g** Co foil, CoS, Co_s-Ru, Co_s-SO-Ru.EXAFS in R-space and corresponding fitting curves for **f** Ru foil, RuO_2,

Co_s-SO-Ru and **g** Co foil, CoS, Co_s-Ru, Co_s-SO-Ru**.** The original EXAFS data are presented without phase correction. *R* represents the distance between the absorbing atoms and neighboring atoms, and $\chi(k)$ denotes the amplitude of the EXAFS oscillations as a function of photoelectron wavenumber *k*.

Supplementary Information, Page 25: "**Supplementary Figure 23.** Detailed EXAFS fitting of Co_s-SO-Ru at Co K-edge, inset curves are the Co-S and Co-S-O path signals (χ_2) involved in the total fitting curve. The original EXAFS data are presented without phase correction."

Supplementary Information, Page 26: "**Supplementary Figure 24. a** XANES spectra taken at Co *K*-edge for CoPc, CoS, and Co_s-SO-Ru. **b** FT-EXAFS in R-space and corresponding fitting curves. The original EXAFS data are presented without phase correction."

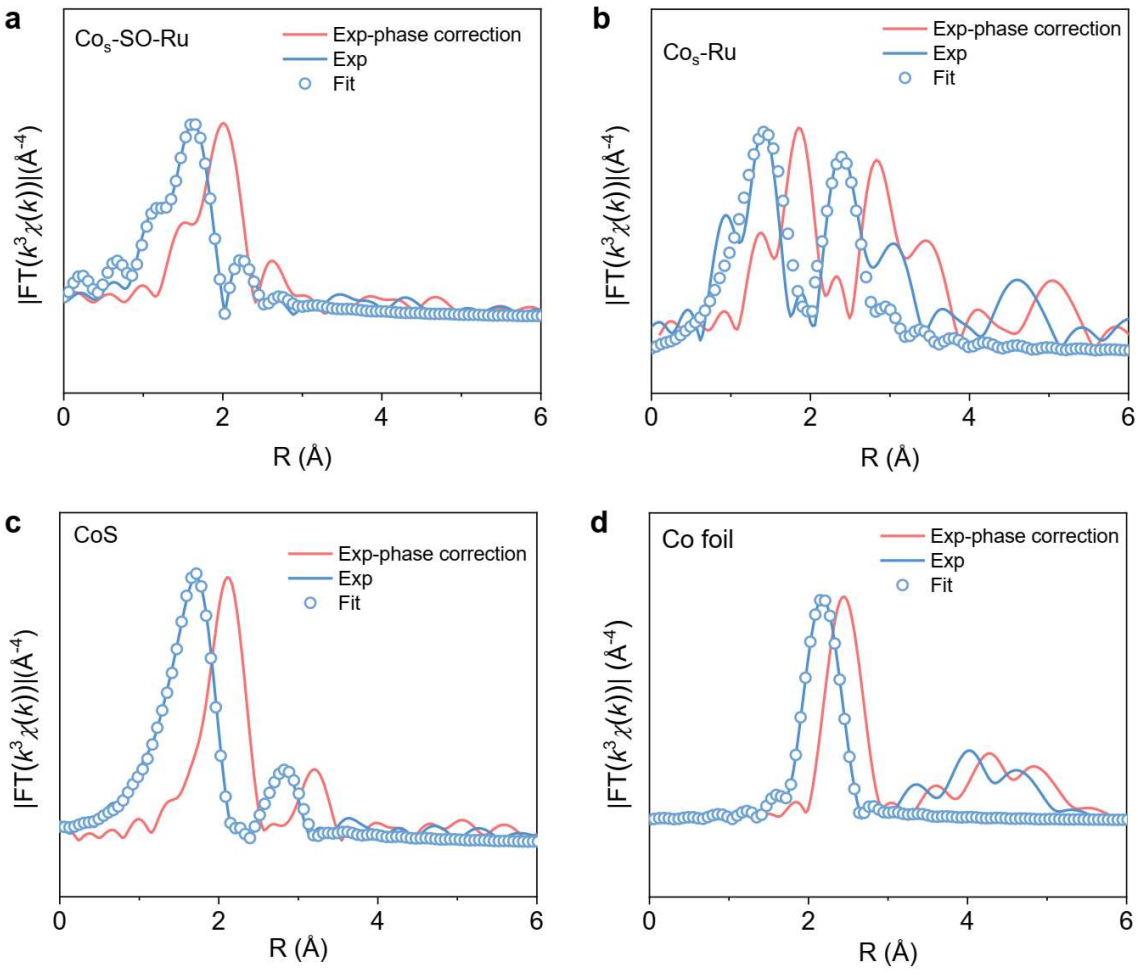


Fig. R1 FT-EXAFS spectra with and without "phase correction" in R-space for **a** Co_s-SO-Ru, **b** Co_s-Ru, **c** CoS, and **d** Co foil.

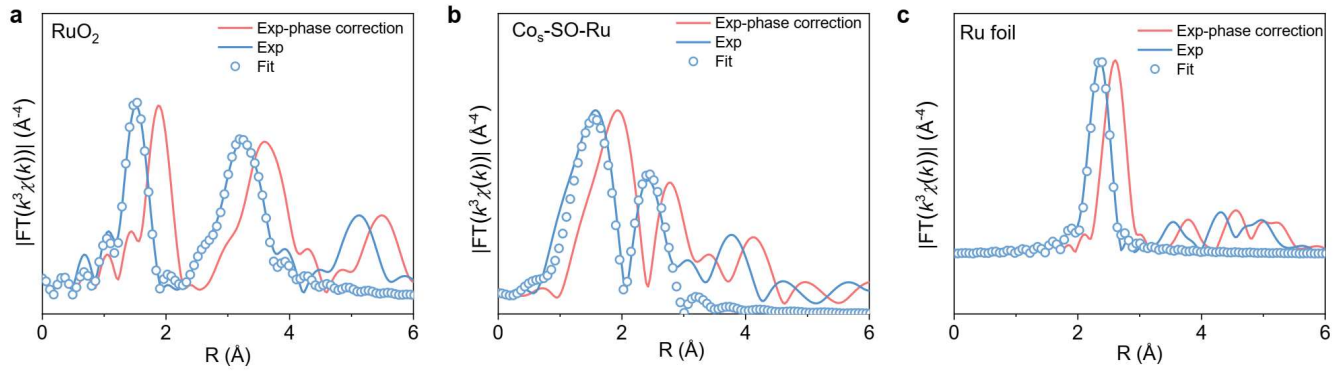


Fig. R2 FT-EXAFS spectra with and without "phase correction" in R-space for **a** RuO_2, **b** Co_s-SO-Ru, **c** Ru foil.

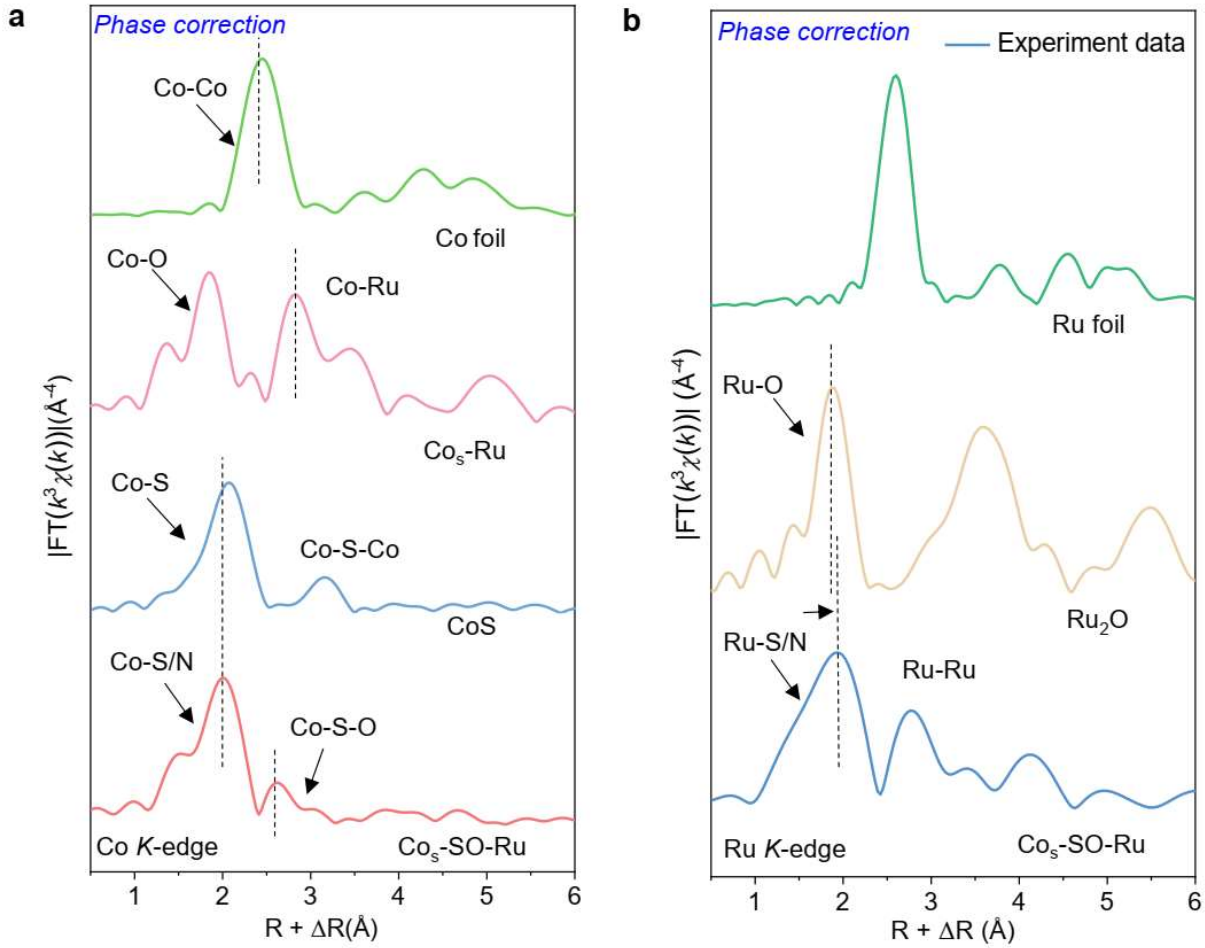


Fig. R3 FT-EXAFS spectra with "phase correction" in R-space for different samples in **a** Co K-edge and **b** Ru K-edge.

[FIGURE REDACTED]

Fig. R4. a FT-EXAFS of different samples in Cu K-edge (***Nature 622, 754–760 (2023).***). **b** Fourier-transformed EXAFS of RuO_2 in Ru K-edge (***Science 387, 48–55 (2025)***). **c** Fourier-transformed EXAFS of different samples in Co K-edge (***Nat. Catal. 7, 702–718 (2024).***). *R* represents the distance between the absorbing atoms and neighboring atoms.

Supplementary Table 3. EXAFS fitting parameters at the Ru *K*-edge for various samples （S_0^2=0.75）

Samples	**shell**	**CN**	**R(Å)**	**σ^2**	**ΔE_0**	**R factor**
Ru foil	Ru-Ru	12	2.68±0.01	0.0041	-4.8±0.7	0.01
RuO_2	Ru-O	5.5±0.6	1.97±0.01	0.0021	4.3±1.7	0.008
	Ru-Ru	7.8±2.6	3.16±0.02	0.0087	4.4±2.5	
	Ru-Ru	4.4±1.3	3.60±0.01	0.0032	12.0±2.5	
Co_s-SO-Ru	Ru-S/N	2.0±1.2	1.99±0.04	0.0070	2.6±4.4	0.023

	Ru-Ru	2.4±0.7	2.68±0.04	0.0134		

[a]*N*: coordination numbers; [b]*R*: bond distance; [c]σ^2: Debye-Waller factors; [d] ΔE_0: the inner potential correction. *R* factor: goodness of fit. S_0^2 was set to 0.75, according to the experimental EXAFS fit of Ru foil reference by fixing CN as the known crystallographic value; δ: percentage.

Supplementary Table 4. EXAFS fitting parameters at the Co *K*-edge for various samples （S_0^2=0.75）

	shell	CN	R(Å)	σ^2	ΔE_0	R factor
Co foil	Co-Co	12	2.49±0.02	0.0063	7.4±0.4	0.001
Co_3O_4	Co-O	5.2±0.5	1.91±0.01	0.0027	-8.1±1.6	0.003
	Co-Co	4.7±1.6	2.86±0.01	0.0038		
	Co-Co	9.1±2.2	3.36±0.01	0.0062		
CoS	Co-S	6.4±0.1	2.21±0.01	0.0089	-8.4±0.4	0.001
	Co-Co	6.0±0.4	3.25±0.01	0.0113		
Co_s-Ru	Co-O	3.0±0.5	1.92±0.02	0.0054	-5.0±2.7	0.020
	Co-Ru	1.0±0.3	2.51±0.09	0.0129		
Co_s-SO-Ru	Co-N	0.8±0.4	1.86±0.05	0.0027	-5.1±2.0	0.003
	Co-S	2.8±0.5	2.23±0.01	0.0141		
	Co-S-O	3.0	2.80±0.03	0.0049		

[a]*N*: coordination numbers; [b]*R*: bond distance; [c]σ^2: Debye-Waller factors; [d] ΔE_0: the inner potential correction. *R* factor: goodness of fit. S_0^2 was set to 0.75, according to the experimental EXAFS fit of Ru foil reference by fixing CN as the known crystallographic value; δ: percentage.

Comment 2: "*From the latest HAADF-STEM and wavelet transform of absorption spectra provided by the author (Supplementary Figure 22), the phenomenon of single atoms is still very obvious. However, due to the author's non-standard "Phase Correction", I am not sure if there is also a problem with the processing of wavelet transform. This requires the author to provide the results of whether each data of*

the absorption spectrum extension edge has and does not have "Phase Correction" before I can infer whether there is a problem with the wavelet transform."

Response: Thank you for this valuable and thoughtful comment. As mentioned in our previous response, the "phase correction" was applied solely to illustrate the phase shift between the peak position (radial distance) in the FT-EXAFS spectra and the actual bond length obtained through fitting. Importantly, wavelet transform (WT) analysis of EXAFS spectra is based on data in k-space and does not involve phase correction procedures (please see the response video).

As widely acknowledged in the literature (e.g., Chem. Soc. Rev., 2024, 53, 11850; Rev. Mineral. Geochem., 2014, 78(1), 33–74), phase correction is not typically applied to either standard FT or WT EXAFS spectra. Consistent with this standard, the FT and WT EXAFS data presented in this study were processed without phase correction to ensure the integrity and accuracy of the spectral analysis.

Comment 3: "*Based on the absorption spectrum data reprocessed by the author, the actual bond length of Co-Coil has shifted to the right. It can be reasonably inferred that other data may also shift to the right after undergoing "Phase Correction"? If that's the case, from the perspective of absorption spectrum, the material is not entirely monatomic. The author cannot attempt to avoid this point by deliberately releasing data that has not undergone "phase correction" to confuse the reader's perspective and attempt to verify single atoms. The author should honestly accept this, acknowledge the impurity of the sample, and focus the article on the characterization of HAADF-STEM and the correlation between structural properties. Or can the author provide other reasonable explanations for this?*"

Response: Thank you for your critical and important comment. As acknowledged in the literature (e.g., Chem. Soc. Rev., 2024, 53, 11850; Rev. Mineral. Geochem., 2014, 78(1), 33–74), phase correction is not typically applied to standard Fourier-transformed (FT) or wavelet-transformed (WT) EXAFS spectra, and doing so may compromise data interpretability. Accordingly, all FT and WT EXAFS spectra in our study were processed without phase correction to ensure data integrity and consistency with established analytical protocols.

The "phase correction" shown in the previous responses was used exclusively for explanatory purposes to help to visualize the phase shift between the apparent peak position in EXAFS and the actual bond lengths obtained from quantitative fitting. It was never used to manipulate the underlying data or alter the interpretation of the coordination environment (Please see the response video).

We fully acknowledge that the sample is not exclusively composed of sulfo-oxygen bridged Co single-atoms on Ru clusters. We did not intend to obscure this point by omitting phase correction; rather, we adhered to the field's norms for processing and interpreting EXAFS data. Therefore, we respectfully clarify that our results are analyzed in accordance with standard methodology. We also appreciate the reviewer's suggestion and have revised the manuscript to more clearly state the phase correction or not.

Comment 4: "*Additionally, please continue to enhance the images and article, as Figure 5f has hardly improved.*"

Response: Thanks. According to your suggestion, we have refined and polished the manuscript to enhance its readability.

Page 5, line 105: "The surface functional groups of carbon black are helpful to anchor possible metal ions and the corresponding counter anion via the electrostatic interaction."

Page 7, line 155: "In contrast, the XANES of Co_s-SO-Ru in Co *K*-edge shows a high-energy position close to Co_3O_4"

Page 7, line 167: "No Co-Co and Co-O-Co peaks can be detected by EXAFS spectrum and WT images, strongly confirming the presence of mononuclear cobalt via sulfo-oxygen bridging with ruthenium sites in Co_s-SO-Ru"

Additionally, the Fig. 2a and Fig. 5f have been revised again, which was shown as follows:

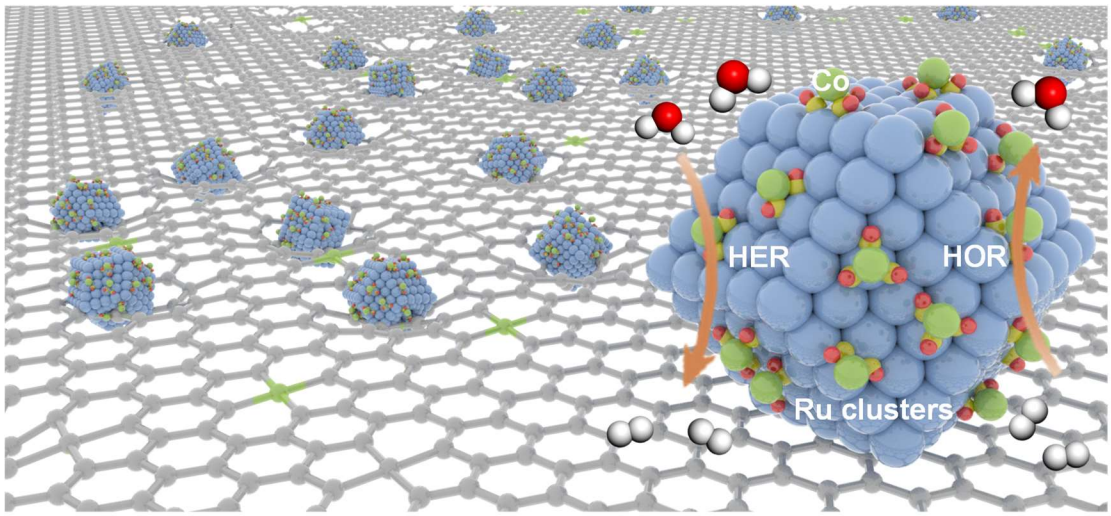


Fig.2 a Schematic illustration of the structure of Co_s-SO-Ru.

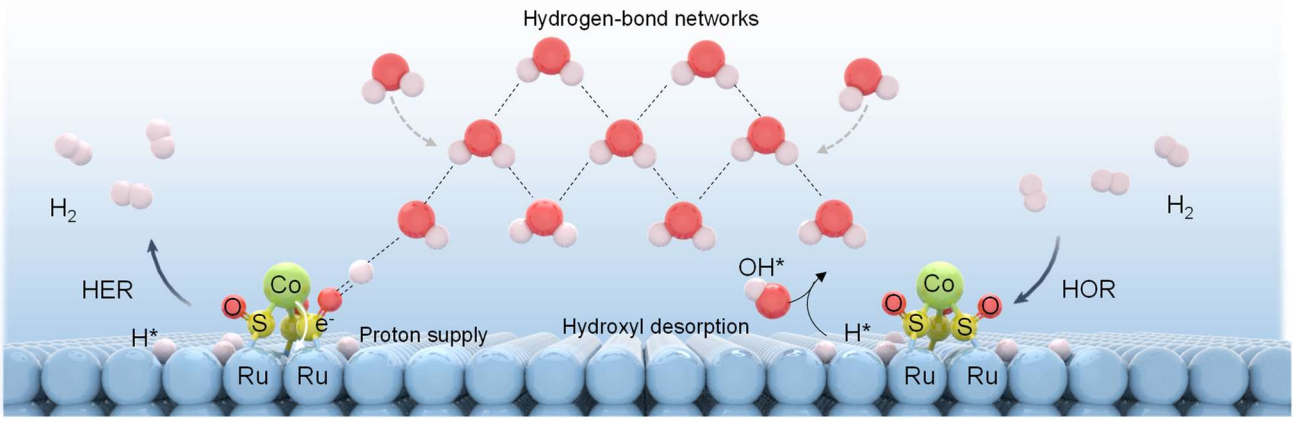


Fig. 5f The schematic illustration of the dynamic hydrogen-bond network conformations.

Reviewer #4: *The authors have answered my comments in full. Therefore, I recommend the publication of the manuscript.*

Response: We sincerely appreciate your kind support and valuable feedback.