

Peer Review File

Operando Visualization of Multi-Site Synergistic H₂-Production Mechanisms on Sub-Nanometric High-Entropy Metallenes



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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

This manuscript entitled “Operando Visualization of Multi-Site Synergistic H₂-Production Mechanisms on Sub-Nanometric High-Entropy Metallenes” demonstrates the synthesis of sub-nanometric high-entropy metallenes (HEMs) with up to eight metallic elements using a universal one-pot wet-chemical approach. Demonstration of the electrocatalytic performance of PdRhMoFeMn HEMs, which exhibit low overpotentials and high stability in different electrolytes. Discovery of synergistic mechanisms in PdRhMoFeMn HEMs, where Mn sites enhance water dissociation at Pd sites with low energy barrier, and Rh sites accelerate hydride coupling for efficient electrocatalytic hydrogen evolution reaction. However, several issues need to be addressed before publication. Detailed comments are as follows:

- On line 106, the authors note that the OH binding energy on the Mn site is -3.05 eV. Consequently, for a reaction mechanism facilitated by Mn, the desorption step of OH from Mn must be included. If OH remains adsorbed on Mn, it cannot be expected to assist the HER. The authors should calculate the rate-determining step and activation energy for this scenario.
- Generally, the sequence of figures should correspond to the order of their description in the text. However, in this manuscript, this sequence is not consistently followed, as seen in the placement of Fig. 2d before Fig. 2c on lines 126 and 129, respectively. This should be searched and corrected.
- Engineering papers typically require quantitative discussion of data that can be quantified. On line 219, the authors claim, “PdRhMoFeMn HEMs have a near-zero onset potential.” This statement should be supported with quantitative data. The same applies to the discussion regarding Figure 4d.
- To enhance readability for readers, the electrochemical data, including those in the supporting information, should be visually modified for clarity. Specifically, the color coding for solid solutions, mono-element metals, and oxides should be uniform, and the lines in the figures should be made thicker for easier identification.
- When discussing XPS analysis, the correlation between specific peak locations and particular species typically requires referencing. For example, authors should refer to appropriate literature like *Advanced Materials* 34.33 (2022): 2204638 for proper citation.
- The TEM-EDS data of senary, octonary, and septenary compounds in Figure S8 show aggregation. The authors should substantiate their claim of successful synthesis of uniform solid solutions. Additionally, they should explain why quinary compounds exhibit superior catalytic activity compared to senary, octonary, and septenary compounds.
- On line 215, the authors mention that PdMoFeMn, RhMoFeMn, and PdRh metallenes are home-made. It should be clarified whether these compounds were synthesized using the same method as PdRhMoFeMn HEM.
- In Figure S31, the lengths of the slabs for each compound differ, which could potentially influence the calculation results. (*The Journal of Chemical Physics* 148.16 (2018)) The authors should either use the same slab for all calculations or explain the necessity for different slabs.
- The term “bigger” on line 344 should be replaced with “higher” for grammatical accuracy.
- The discussion on operando XANES and EXAFS data lacks clarity regarding the specific reaction mechanism corresponding to the observed changes in XANES and EXAFS. This should be precisely presented.
- Given that Mn is presented as the OH binding site in the introduction, it is essential to include

operando XAS results of Mn.

- On lines 411-413, the authors suggest that the increase in intensity of Pd-O during potential drop is due to water adsorption on Pd-O. However, on lines 413-415, they state that the increase in Pd-Pd intensity is due to OH desorption. This appears contradictory. It is necessitated that a detailed description of the reactions occurring at the Pd site during the potential drop.

- The reasons for the high stability of the developed catalysts should be discussed. If the stability is attributed to the high configurational entropy of the HEM, a comparison with senary, octonary, and septenary compounds, which are expected to have higher configurational entropy, should be made.

Reviewer #2 (Remarks to the Author):

In this manuscript, the authors reported a high-entropy metallenes (HEMs) material as HER catalyst. There are lots of experimental and computational results in this work. However, the authors made some mistakes in computational part and the reviewer had to reject this manuscript. The comments from the reviewer have been shown below.

1. In computational method, the authors mentioned that the free energy was calculated using the equation ' $G = E + ZPE - TS$ '. It is a correct equation to calculate free energy. However, based on the data in supplementary Table 5, the free energy is calculated using equation ' $G = E - ZPE - TS$ '. Please double check these results. Considering that the free energy of adsorbed H is the most important factor to predict the activity of HER, most of DFT predictions will be invalid if equation is incorrect.

2. Also, in supplementary Table 5, the calculated ZPE for *H on different sites is ranging from 0.018 to 0.225 eV. Considering that the same adsorption configuration will lead to close ZPE value, the reviewer is surprised by the ZPE difference of ~ 0.2 eV on different HEM sites. Please check these results, especially the ZPE for *H on Pd₂ site. Moreover, please also check the adsorption configuration of H after structure relaxation. If the adsorption configuration changes from top site to hollow site, please mention it in manuscript.

3. In computational method, the DFT + U method was adopted in this work. Generally, the DFT + U is used to correct the energy for the system with strongly correlated electrons or localized electrons, like many metal oxide system. As for the metal or alloy system, it is not necessary to introduce DFT + U. Please explain why adopting DFT + U method in this work to model high-entropy metallenes.

4. In 321st line of the manuscript, the authors mentioned that the 'Bader charge value of xx is xx'. The output of bader charge analysis is a table showing the number of electrons for each atom and this result mainly exhibits the electronic transfer/interaction in system. Therefore, the reviewer is confused about the definition of 'bader charge value' and please provide how to calculate the bader charge value. Moreover, please explain why a higher bader charge value represents a higher electrical conductivity.

Reviewer #3 (Remarks to the Author):

This manuscript shows a chemical synthesis method to produce nano-meter sized high-entropy

metallenes (containing PdRhMoFeMn). This material shows low overpotentials for HER in both acidic and alkaline conditions as well as high stability.

This approach is similar to previously published work. For example, Zhang et al in *Electrochimica Acta* 279, pages 19-23, showed that their high entropy alloy (Ni Fe Mo Co Cr) had excellent activity under both acidic and alkaline conditions as well as high stability. Furthermore, this high entropy alloy was free of any PGM. Similarly, the work by Li et al in *Nature Communications* (article number 5437) shows how a high entropy alloy containing one PGM, PtNiFeCoCu, reaches the same HER activity as that reported in the current manuscript, again both at acidic and alkaline conditions. And very recently, the work by Kang et al, *Nature Communications*, article number 4182, showed that PtPdRhRuCu also reached similar activities for HER and stability as reported here. In conclusion, the here proposed concept to use a high entropy material, although of different composition, is not of high enough novelty that it warrants publication in *Nature Communications*.

So maybe this work, as promised by the title, provides additional insight in the role of the different elements under operando conditions through operando XAS? The answer here is: not really

- How quickly after setting the potential were the operando XAS spectra measured (i.e. was this done consistently and how long does it take to collect a spectrum)?
- What do the Mo and Fe XANES spectra show?
- The observed shifts in the Pd and Rh XANES spectra are extremely small, and as made very clear in the pre-edge background in Figure 6e, could just be the result of non-consistent normalization. What is done to warrant absolute energy calibration? Also, what is the feature at 24319 eV in Figure c? Could it be that you have bubble formation that distorted your XANES spectra? You should have electrolyte flow in your cell to bring away bubbles.
- The potential reduction of the white line intensity for Pd could also be the result of a slight oxidation at higher pH, rather than an increase in electron density on the Pd atom. Please show a larger portion of your XANES spectra.
- Figure 7 suggests significant Pd-Pd and Rh-Rh scattering, suggesting that you do not form homogeneous metallenes.
- Also in Figure 7 c and e there is a significant increase in the Pd K-edge XAFS background observed (suggesting quite different noise levels) which then also leads to an increase in intensity of spectral features that you assign to Pd-O. Are spectra collected and treated consistently? Please show the k-space EXAFS spectra as well. Based on what do you assign oxygen contributions to the Pd K-XAS spectra? Did you attempt to fit the spectra?
- Can you please explain the lower intensity between 1 and 2 Å in figure 7f vs 7 b and d? Could it be that you have an oxygen contribution there? Without fitting your EXAFS spectra the assignments made and the discussion of the results is very speculative.
- DFT calculations assume a perfectly mixed alloy, but there is no proof that this is actually the case. Rather do your operando EXAFS results with a Rh-Rh and Pd-Pd scattering peak (see operando XAS results) suggest that there is local cluster formation in your materials. In contrast though, your ex situ characterization suggests that you have a mixture of nearest neighbours. Did you attempt to fit your EXAFS spectra? What about the many vacancies in the structure, observed by TEM, but not taken into account in the calculations?

The role of Rh, Pd and Mn at various pH conditions has been made clear, mostly by electrocatalytic tests. However, the role of Mo and Fe is not obvious. Why are these elements needed?

Minor comments:

You have also prepared materials containing even more elements, including Ir. Why were there materials not tested and characterized for HER?

Stability tests have been made to show that the material is quite stable. Can you please provide the same physical chemical characterization of the PdRhMoFeMn material after the stability tests? i.e., are all elements stable, or do some elements preferentially leach out? Also, there is a large discrepancy in the elemental analysis by SEM-EDS and ICP-OES for Rh, please address this.

Lines 351-355: There is a disconnect between your experimental data, which suggest Pd is the active site at higher pH and the DFT calculations (the ΔG descriptor) that suggests Rh is the active site over the whole pH range. How much stock should we put in these DFT calculations (and what is the relevance of thermal stability calculations)?

Response to Decision Letter

February 3, 2024

Journal: Nature Communications

Reference number: NCOMMS-23-58688

Title: Operando Visualization of Multi-Site Synergistic H₂-Production Mechanisms on Sub-Nanometric High-Entropy Metallenes

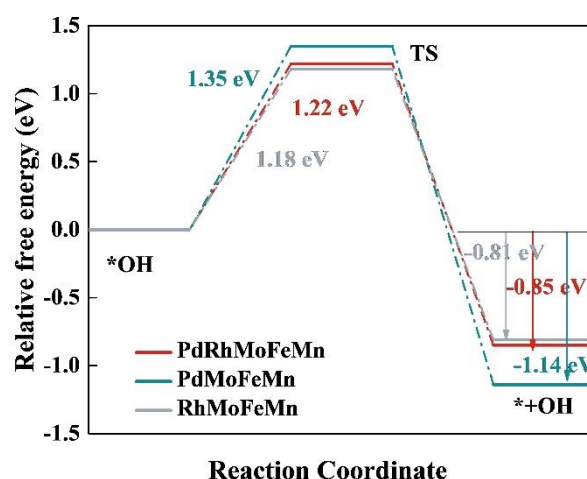
Reviewer #1 (Remarks to the Author):

This manuscript entitled “Operando Visualization of Multi-Site Synergistic H₂-Production Mechanisms on Sub-Nanometric High-Entropy Metallenes” demonstrates the synthesis of sub-nanometric high-entropy metallenes (HEMs) with up to eight metallic elements using a universal one-pot wet-chemical approach. Demonstration of the electrocatalytic performance of PdRhMoFeMn HEMs, which exhibit low overpotentials and high stability in different electrolytes. Discovery of synergistic mechanisms in PdRhMoFeMn HEMs, where Mn sites enhance water dissociation at Pd sites with low energy barrier, and Rh sites accelerate hydride coupling for efficient electrocatalytic hydrogen evolution reaction. However, several issues need to be addressed before publication. Detailed comments are as follows:

Response: We would like to thank the reviewer for the valuable comments and suggestions. Based on your comments and suggestions, we have revised our manuscript carefully. All changes have been highlighted in the revised manuscript by formatting the text in Yellow color. Detailed lists of revisions are listed below:

Q1. On line 106, the authors note that the OH binding energy on the Mn site is -3.05 eV. Consequently, for a reaction mechanism facilitated by Mn, the desorption step of OH from Mn must be included. If OH remains adsorbed on Mn, it cannot be expected to assist the HER. The authors should calculate the rate-determining step and activation energy for this scenario.

Response: Thanks for your helpful suggestion. The transition state of OH desorption kinetics on Mn was calculated as shown in Supplementary Figs. 41. It reveals that the OH desorption energy of PdRhMoFeMn at Mn sites was -0.85 eV, which falls between RhMoFeMn (-0.81 eV) and PdMoFeMn (-1.14 eV), indicating its proximity to RhMoFeMn and demonstrating favorable desorption performance.



Supplementary Fig. 41 The calculated transition state of OH desorption kinetics at the Mn sites of PdRhMoFeMn, PdMoFeMn and RhMoFeMn.

Changes to the main text:

Line 383: Moreover, Fig. 5g and Supplementary Figs. 41 shows that the Mn atom has the highest binding energy to hydroxyl groups among the atoms in PdRhMoFeMn HEMs and the favorable OH desorption energy of PdRhMoFeMn at Mn sites is -0.85 eV, which can accelerate water dissociation into H and OH intermediates, followed by the reaction on the Rh site to produce H₂.

Q2. Generally, the sequence of figures should correspond to the order of their description in the text. However, in this manuscript, this sequence is not consistently followed, as seen in the placement of Fig. 2d before Fig. 2c on lines 126 and 129, respectively. This should be searched and corrected.

Response: Thanks for your valuable suggestion. According to your comments, we have carefully checked the sequence of figures and corrected these errors in this manuscript.

Q3. Engineering papers typically require quantitative discussion of data that can be quantified. On line 219, the authors claim, “PdRhMoFeMn HEMs have a near-zero onset potential.” This statement should be supported with quantitative data. The same applies to the discussion regarding Figure 4d.

Response: Thanks for your professional suggestion! According to your comments, we have carefully revised and conducted a quantitative analysis of these data.

Changes to the main text:

Line 226: The HER polarization curves with iR-compensation in Fig. 4a show that PdRhMoFeMn HEMs have a near-zero onset potential (-0.16 mV) and only require a η_{10} of 6 mV, lower than those of RhMoFeMn metallenes (20 mV), PdRh metallenes (16 mV), and Pt/C (13 mV).

Line 252: As illustrated in Fig. 4d, the polarization curves of PdRhMoFeMn HEMs before and after 10,000 cyclic voltammetry (CV) cycles remain virtually unchanged and the η_{100} of PdRhMoFeMn HEMs increases only 1 mV after 10,000 cycles.

Q4. To enhance readability for readers, the electrochemical data, including those in the supporting information, should be visually modified for clarity. Specifically, the color coding for solid solutions, mono-element metals, and oxides should be uniform, and the lines in the figures should be made thicker for easier identification.

Response: Thanks for your valuable suggestion. According to your comments, we have carefully revised all the electrochemical data in this manuscript to improve its readability for readers. In detail, we have kept the colors consistent for each sample and bolded all lines in Fig. 4 and Supplementary Figs. 16-28 to make the information easier for readers to access.

Q5. When discussing XPS analysis, the correlation between specific peak locations and particular species typically requires referencing. For example, authors should refer to appropriate literature like Advanced Materials 34.33 (2022): 2204638 for proper citation.

Response: Thanks for your helpful comments here. Based on it, we have added corresponding references to the XPS discussion to support our data analysis and conclusions.

Changes to the main text:

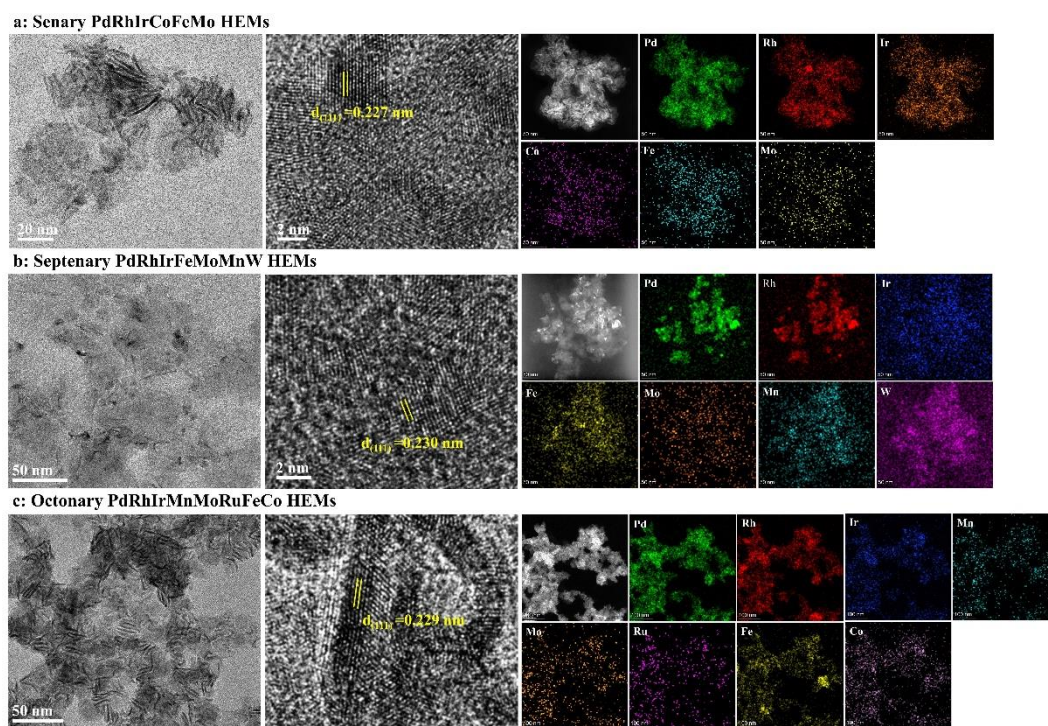
Line 175: The surface chemical composition of PdRhMoFeMn HEMs was further investigated with X-ray photoelectron spectroscopy (XPS) (ACS Catalysis 12, 15045-15055 (2022); Advanced Materials 34, 2204638 (2022); Nature Communications 13, 2807 (2022)). The XPS survey spectrum identifies that Pd, Rh, Mo, Fe, and Mn elements coexist in HEMs (Supplementary Fig. 6a). The Pd 3d XPS spectrum reveals the presence of main metallic Pd and a small amount of palladium oxide, in which the peaks at 334.83 and 340.14 eV correlate to Pd⁰ 3d_{5/2} and Pd⁰ 3d_{3/2}, respectively (Fig.

3e) (Advanced Materials 35, 2208860 (2023)). The peaks at 336.08 and 341.47 eV match $\text{Pd}^{2+} 3d^{5/2}$ and $\text{Pd}^{2+} 3d^{3/2}$ (Angewandte Chemie-International Edition 60, 12027-12031 (2021)). Similarly, the majority of Rh exists as a zero-valence substance, with a small proportion as a 1+ or 3+ substance (Fig. 3f). In detail, the high-resolution Rh 3d spectra of PdRhMoFeMn HEMs are composed of six fitting peaks of $\text{Rh}^0 3d_{5/2}$ (306.59 eV), $\text{Rh}^0 3d_{3/2}$ (311.31 eV), $\text{Rh}^+ 3d_{5/2}$ (307.54 eV), $\text{Rh}^+ 3d_{3/2}$ (312.58 eV), $\text{Rh}^{3+} 3d_{5/2}$ (312.86 eV) and $\text{Rh}^{3+} 3d_{5/2}$ (653.67 eV) (ACS Nano 17, 10733-10747 (2023)).

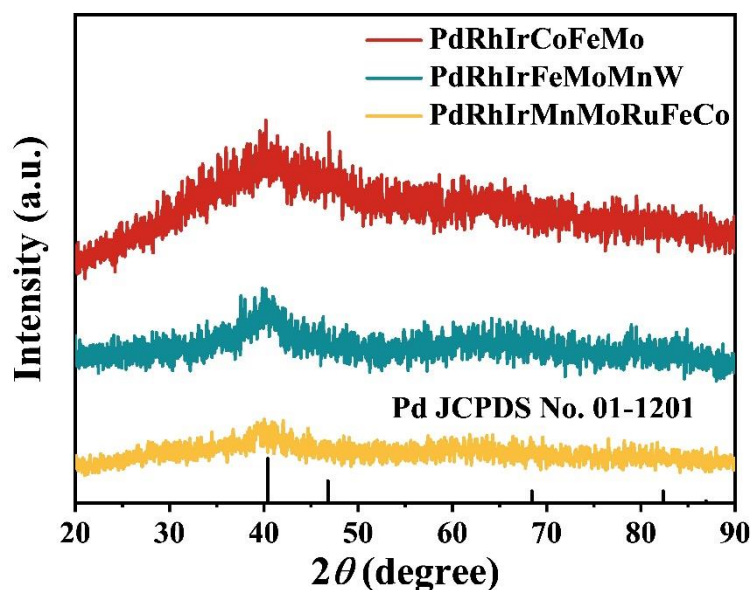
Q6. The TEM-EDS data of senary, octonary, and septenary compounds in Figure S8 show aggregation. The authors should substantiate their claim of successful synthesis of uniform solid solutions. Additionally, they should explain why quinary compounds exhibit superior catalytic activity compared to senary, octonary, and septenary compounds.

Response: Thanks for your insightful comment here. We agree that better dispersion and higher resolution TEM-EDS data can help to demonstrate the successful preparation of uniform HEMs more directly. However, due to the ultra-thin (1-1.5 nm) structure and small size of the HEMs and limited by the effective resolution of the available HRTEM equipment, it is difficult for us to obtain monodisperse high-resolution TEM-EDS data. To confirm the successful preparation of uniform HEMs, we have added some characterization and more detailed analysis in the main text and Supporting Information. Specifically, we have added corresponding higher resolution HRTEM images of senary, octonary, and septenary HEMs to prove the formation of uniform high-entropy metallenes. The HRTEM images in Supplementary Fig. 8 show that there was no formation of nanoparticles or clusters on the surfaces of senary, octonary, and septenary HEMs, proving that all metal atoms are well mixed within the metallenes. They also display clear lattice fringes with lattice distances of 0.227, 0.230, and 0.229 nm, corresponding to the {111} facets of senary, octonary, and septenary HEMs, respectively. Their element ratios were further determined by the SEM-EDS (Supplementary Fig. 10). The content of each element in their corresponding catalysts ranges from 5-35%, which meets the definition of a high-

entropy alloy. Importantly, the XRD results of senary, octonary, and septenary HEMs in Supplementary Fig. 11 indicate that they have a face-centered cubic structure without phase segregation, similar to pure Pd. The broadening and weakening of their XRD peaks and the shift of peak positions relative to pure Pd are due to the introduction of other metal elements, which directly proves the successful formation of single-phase HEMs. The above-mentioned methods confirming the successful preparation of uniform high-entropy solid solutions are also consistent with the reported literature like *Angewandte Chemie-International Edition* 135, e202217976 (2023), *Advanced Materials* 35, 2209242 (2023), and *Journal of the American Chemical Society* 144, 10582-10590 (2022).

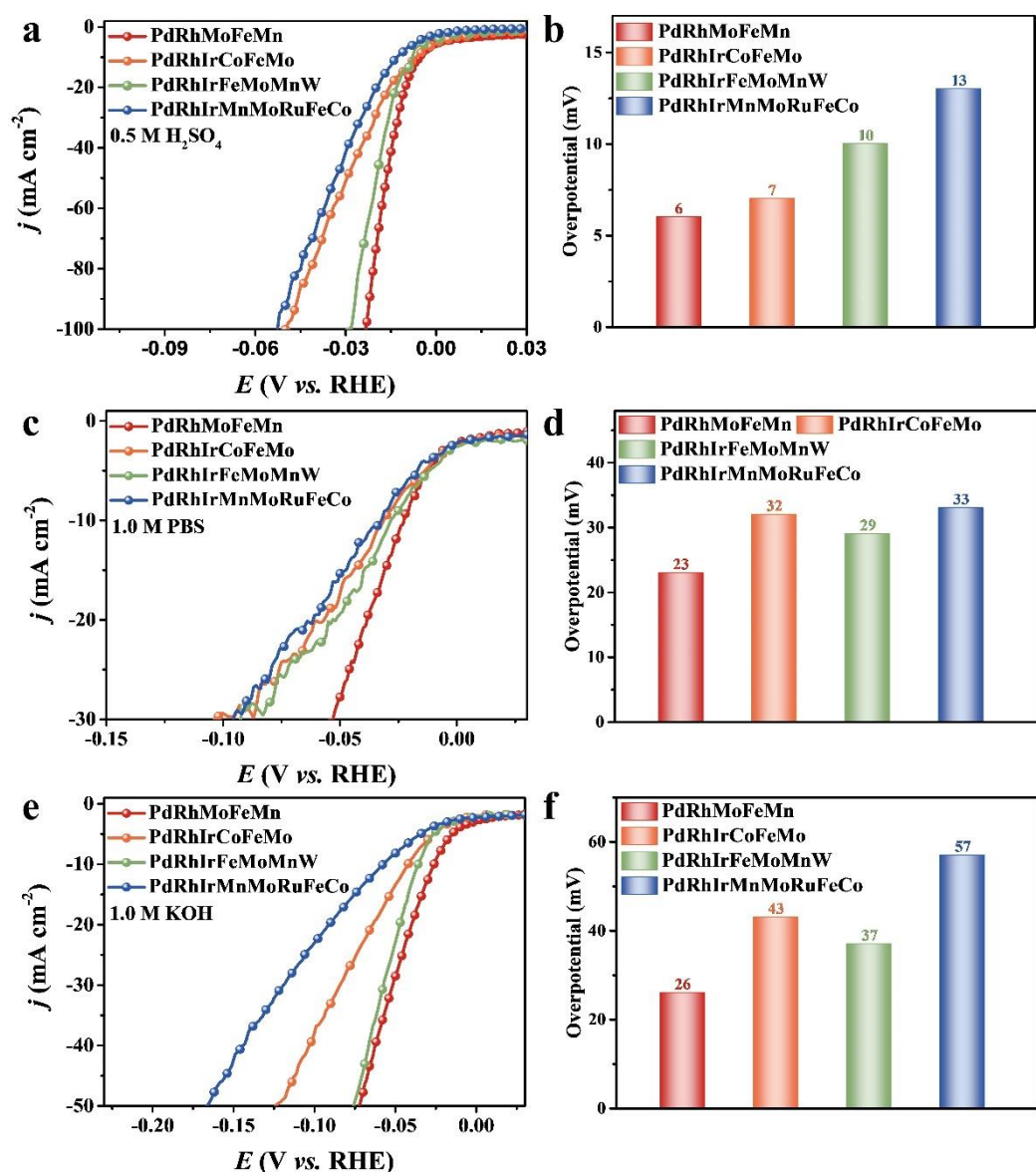


Supplementary Fig. 8 TEM, HRTEM, and EDS elemental mapping images of HEMs with different compositions. TEM, HRTEM, and EDS elemental mapping images of **(a)** senary PdRhIrCoFeMo HEMs, **(b)** septenary PdRhIrFeMoMnW HEMs, and **(c)** octonary PdRhIrMnMoRuFeCo HEMs.



Supplementary Fig. 11 XRD patterns of senary PdRhIrCoFeMo HEMs, septenary PdRhIrFeMoMnW HEMs, and octonary PdRhIrMnMoRuFeCo HEMs.

According to your comments, we have supplemented the HER performance tests of senary PdRhIrCoFeMo, septenary PdRhIrFeMoMnW, and octonary PdRhIrMnMoRuFeCo HEMs and compared them to quinary PdRhMoFeMn HEMs. As shown in Supplementary Fig. 27, quinary PdRhMoFeMn HEMs exhibit the low η_{10} values of 6, 23 and 26 mV, superior to senary PdRhIrCoFeMo HEMs (7, 32 and 43 mV), septenary PdRhIrFeMoMnW HEMs (10, 29 and 37 mV), and octonary PdRhIrMnMoRuFeCo HEMs (13, 33 and 57 mV) in 0.5 M H₂SO₄, 1.0 M PBS, and 1.0 M KOH electrolytes, respectively. The reasons for the higher activity of quinary HEMs are as follows: First, the thickness of quinary HEMs is only about 1.0 nm, which is thinner than that of senary (1.33 nm), septenary (1.40 nm) and octonary (1.46 nm) HEMs, indicating more exposed active sites and higher atomic utilization efficiency. Furthermore, Rh and Pd active components that are highly effective for HER have higher content in quinary HEMs compared to other HEMs.



Supplementary Fig. 27 Electrocatalytic HER performance evaluation of quinary PdRhMoFeMn, senary PdRhIrCoFeMo, septenary PdRhIrFeMoMnW, and octonary PdRhIrMnMoRuFeCo HEMs. (a) Polarization curves and (b) corresponding overpotentials at 10 mA cm⁻² of HEMs with different composition in 0.5 M H₂SO₄. (c) Polarization curves and (d) corresponding overpotentials at 10 mA cm⁻² of HEMs with different composition in 1.0 M PBS. (e) Polarization curves and (f) corresponding overpotentials at 10 mA cm⁻² of HEMs with different composition in 1.0 M KOH.

Changes to the main text:

Line 204: HRTEM images show that there was no formation of nanoparticles or

clusters on the surfaces of senary, octonary, and septenary HEMs, proving that all metal atoms are well mixed within the metallenes. They also display clear lattice fringes with lattice distances of 0.227, 0.230, and 0.229 nm, corresponding to the {111} facets of senary, octonary, and septenary HEMs, respectively.

Line 211: In addition, the XRD pattern shows that all HEMs have an *fcc* alloy structure without phase separation. The broadening and weakening of their peaks and the shift of peak positions relative to pure Pd are due to the introduction of other metal elements, proving the successful formation of single-phase HEMs (Supplementary Fig. 11).

Line 320: Additionally, the HER performance of quinary PdRhMoFeMn HEMs were also compared with that of senary PdRhIrCoFeMo, septenary PdRhIrFeMoMnW, and octonary PdRhIrMnMoRuFeCo HEMs. As shown in Supplementary Fig. 26, PdRhMoFeMn HEMs exhibit smaller overpotential than senary, septenary, and octonary HEMs at the same current density under acidic, neutral, and alkaline environments due to better atomic utilization efficiency and active site configurations.

Q7. On line 215, the authors mention that PdMoFeMn, RhMoFeMn, and PdRh metallenes are home-made. It should be clarified whether these compounds were synthesized using the same method as PdRhMoFeMn HEM.

Response: Thanks for your helpful suggestions here. According to your comments, we have clarified the preparation method of PdMoFeMn, RhMoFeMn, and PdRh metallenes in the main text. They were synthesized using the same method as PdRhMoFeMn HEMs except for varying the kinds of metallic precursors.

Changes to the main text:

Line 221: For comparison, the HER performance of PdMoFeMn (Supplementary Fig. 12), RhMoFeMn (Supplementary Fig. 13), and PdRh metallenes (Supplementary Fig. 14) synthesized by the same preparation method as PdRhMoFeMn HEMs, and Pt/C catalysts were also investigated as reference substances under the same electrochemical test conditions.

Line 506: For the synthesis of RhMoFeMn, PdMoFeMn, and PdRh metallenes, all the conditions were the same as those of PdRhMoFeMn HEMs except for varying the

kinds of metallic precursors.

Q8. In Figure S31, the lengths of the slabs for each compound differ, which could potentially influence the calculation results. (The Journal of Chemical Physics 148.16 (2018)) The authors should either use the same slab for all calculations or explain the necessity for different slabs.

Response: Thanks for your comments here. All simulated catalysts were calculated in this manuscript with the same cell parameters ($a=b=10.58010 \text{ \AA}$, $c=21.84430 \text{ \AA}$), which is described in detail in the section of computation methods in Supplementary Information. There may be some difference between the angle of the model and the atomic magnification that makes your vision different. We apologize for any confusion this may have caused.

Q9. The term “bigger” on line 344 should be replaced with “higher” for grammatical accuracy.

Response: We sincerely thank the reviewer for careful reading. As suggested by the reviewer, we have corrected the “bigger” into “higher” in the main text.

Changes to the main text:

Line 360: Meanwhile, the integrated COHP (ICOHP) value for Rh in PdRhMoFeMn with H_2 (-0.89 eV) is higher than that of Rh in RhMoFeMn (-1.17 eV), and Rh in PdRh (-1.34 eV), suggesting the increased antibonding-orbital occupancy in the PdRhMoFeMn than those in PdRh and RhMoFeMn and the increased difficulty for the H_2 adsorption at Rh sites in PdRhMoFeMn (Fig. 5d).

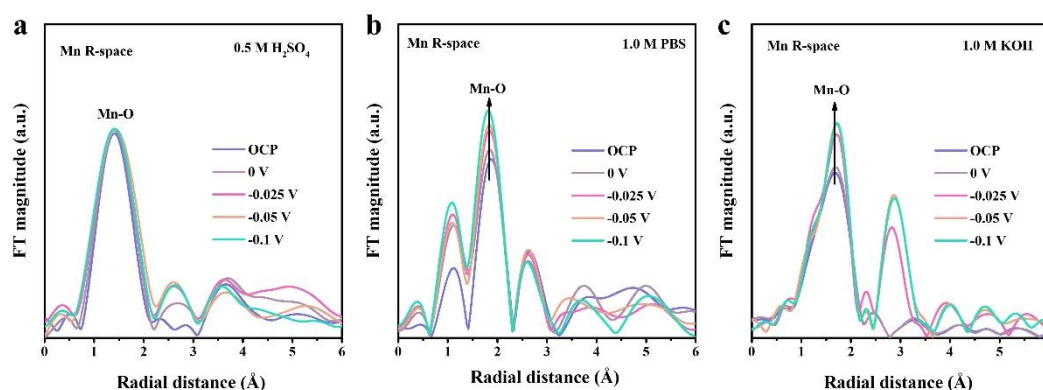
Q10. The discussion on operando XANES and EXAFS data lacks clarity regarding the specific reaction mechanism corresponding to the observed changes in XANES and EXAFS. This should be precisely presented.

Response: We sincerely thank the reviewer for the constructive comments. Firstly, we observed changes in the charge density of Rh, Pd, and Mn in the XANES spectra, as shown in Fig. 6 and Supplementary Fig. 47. Based on these observations, we attempted to propose a reaction mechanism, with Rh identified as the primary reaction site at various pH values, while Mn assists in the hydrolysis at Pd sites under KOH and PBS conditions. Furthermore, in the EXAFS spectra of Rh, Pd, and Mn (Fig. 7 and Supplementary Fig. 48), we observed their changes in the atomic environment.

Particularly, Rh remained unchanged, primarily due to its reaction with H^* . Therefore, the observed variations in electron density align with the XANES results. For Pd sites, we observed slight changes in Pd-O under KOH and PBS conditions, demonstrating its involvement in the hydrogen reaction evolution. The increase in Mn-O only under alkaline and neutral conditions suggests the generation of more hydroxyl groups at the Mn sites.

Q11. Given that Mn is presented as the OH binding site in the introduction, it is essential to include operando XAS results of Mn.

Response: Thank the reviewer for your professional advice. We have added in situ Mn data for each electrolyte, and it is observed that under reducing potentials, only alkaline and neutral conditions show an increase in manganese-oxygen (Mn-O). This suggests the generation of more Mn-OH. In acidic conditions, Mn-O remains nearly unchanged. This result indicates that the OH produced by the H_2O dissociation step is transferred and adsorbed to the Mn site, thus accelerating the H_2O dissociation at the Pd site.



Supplementary Fig. 48 Operando EXAFS spectra of Mn at various potentials in (a) 0.5 M H_2SO_4 , (b) 1.0 M KOH, and (c) 1.0 M PBS solutions.

Changes to the main text:

Line 431: Specifically, for the Mn site, an increase in Mn-O is observed only under alkaline and neutral conditions, suggesting the generation of more hydroxyl groups at the Mn sites (Supplementary Fig. 48c,d). In acidic conditions, Mn-O remains nearly unchanged (Supplementary Fig. 48a).

Q12. On lines 411-413, the authors suggest that the increase in intensity of Pd-O

during potential drop is due to water adsorption on Pd-O. However, on lines 413-415, they state that the increase in Pd-Pd intensity is due to OH desorption. This appears contradictory. It is necessitated that a detailed description of the reactions occurring at the Pd site during the potential drop.

Response: Thank you for the detailed review. Firstly, the increase in Pd-M (Pd-Pd/Mo/Rh/Fe/Mn) intensity implies an enhancement in charge density (consistent with what we observed in XANES), and this elevated charge density facilitates the acceleration of water adsorption and dissociation (Volmer step). Subsequently, we observed an accompanying increase in Pd-O intensity, demonstrating that Pd serves as an active site for water dissociation. We have incorporated the detailed corrections into the manuscript.

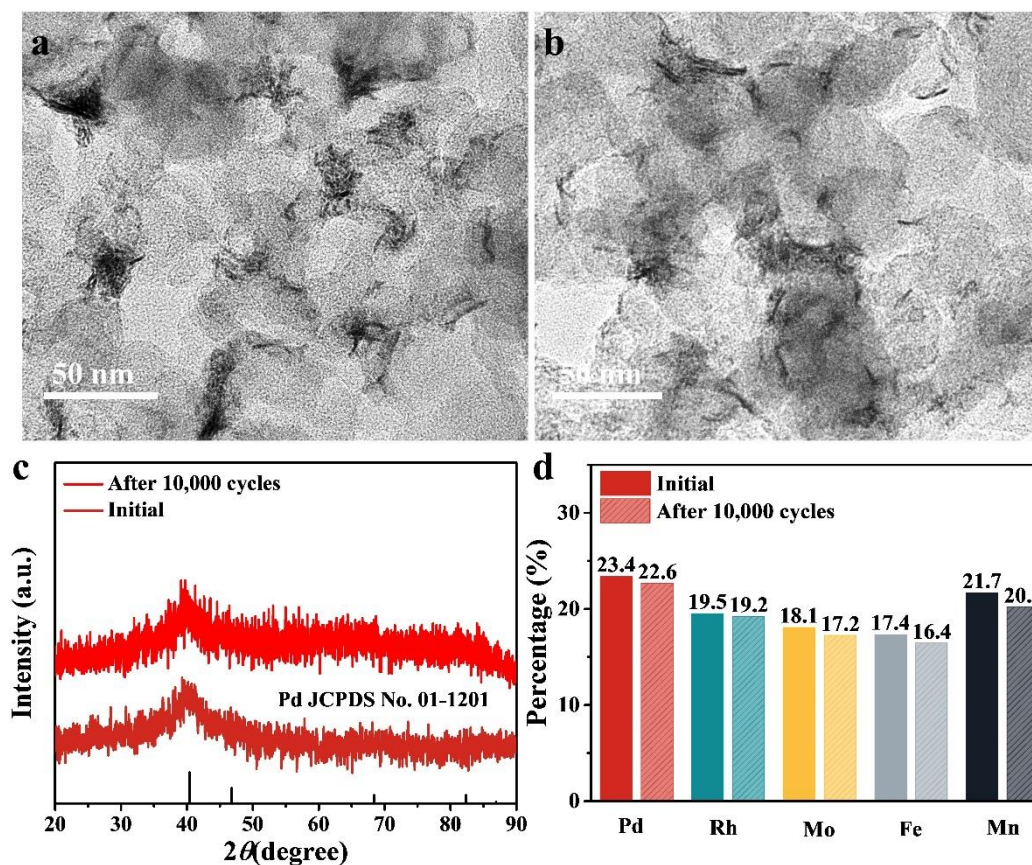
Changes to the main text:

Line 439: At the same time, the gradual increase in the Pd-M peak at 2.5 Å suggests the slightly increasing presence of metallic Pd sites, implies an enhancement in charge density (consistent with what we observed in XANES), and this elevated charge density facilitates the acceleration of water adsorption and dissociation, favoring the Volmer step.

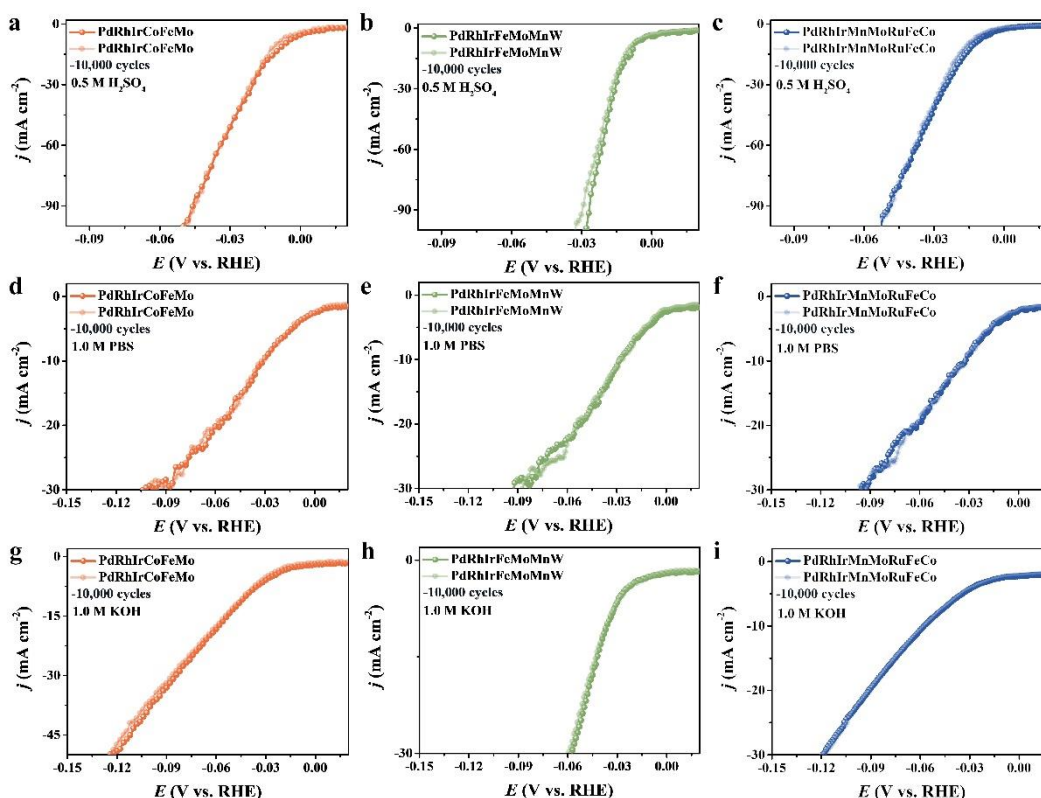
Q13. The reasons for the high stability of the developed catalysts should be discussed. If the stability is attributed to the high configurational entropy of the HEM, a comparison with senary, octonary, and septenary compounds, which are expected to have higher configurational entropy, should be made.

Response: Thanks for your constructive suggestions here. Based on it, we have supplemented TEM, XRD, and ICP-OES tests before and after stability to explore the reasons for its high stability. As shown in Supplementary Fig. 18a,b, the morphology of nanosheet was well maintained. The catalyst is still well dispersed on the carbon and there is no significant aggregation. XRD and ICP-OES results indicate that the crystal structure and composition of PdRhMoFeMn HEMs have not changed obviously, further suggesting their robustness (Supplementary Fig. 18c,d). In addition, we also supplemented the HER stability tests of senary, septenary, and octonary HEMs. All these HEMs exhibit small negative shifts after 10,000 CV cycles, indicating their excellent electrochemical stability (Supplementary Fig. 28). Therefore,

the excellent durability of PdRhMoFeMn HEMs is due to the stability of morphological structure and high entropy effect.



Supplementary Fig. 18 Characterizations of PdRhMoFeMn HEMs before and after 10,000 CV cycles. TEM images (a) before and (b) after 10,000 CV cycles. (c) XRD pattern before and after 10,000 CV cycles. (d) ICP-OES results before and after 10,000 CV cycles.



Supplementary Fig. 28 Electrochemical HER stability tests of senary PdRhIrCoFeMo, septenary PdRhIrFeMoMnW, and octonary PdRhIrMnMoRuFeCo HEMs. The polarization curves of (a) senary HEMs, (b) septenary HEMs, and (c) octonary HEMs before and after 10,000 CV cycles in 0.5 M H₂SO₄. The polarization curves of (d) senary HEMs, (e) septenary HEMs, and (f) octonary HEMs before and after 10,000 CV cycles in 1.0 M PBS. The polarization curves of (g) senary HEMs, (h) septenary HEMs, and (i) octonary HEMs before and after 10,000 CV cycles in 1.0 M KOH.

Changes to the main text:

Line 260: Besides, the TEM images show that PdRhMoFeMn HEMs maintain the nanosheet shape and the distribution on the carbon is still uniform without aggregation (Supplementary Fig. 18a,b). XRD results in Supplementary Fig. 18c suggest that (111) facet-dominated fcc structure could be well retained after 10,000 cycles. Moreover, the ICP-OES characterizations before and after 10,000 cycles further indicate that there was no obvious change in the composition of PdRhMoFeMn HEMs, further suggesting their robustness (Supplementary Fig. 18d).

Line 326: Particularly, all these HEMs exhibit small negative shifts after 10,000 CV cycles, indicating their excellent electrochemical stability (Supplementary Fig. 28).

Finally, we hope that all concerns have been addressed. Thank you very much again for your attention and kindness to improve our work.

Reviewer #2 (Remarks to the Author):

In this manuscript, the authors reported a high-entropy metallenes (HEMs) material as HER catalyst. There are lots of experimental and computational results in this work. However, the authors made some mistakes in computational part and the reviewer had to reject this manuscript. The comments from the reviewer have been shown below.

Response: We would like to thank you for your constructive suggestions on our work. Based on your comments and suggestions, we have revised our manuscript carefully. All changes have been highlighted in the revised manuscript by formatting the text in Yellow color. Detailed lists of revisions are listed below:

Q1. In computational method, the authors mentioned that the free energy was calculated using the equation ' $G = E + \text{ZPE} - TS$ '. It is a correct equation to calculate free energy. However, based on the data in supplementary Table 5, the free energy is calculated using equation ' $G = E - \text{ZPE} - TS$ '. Please double check these results. Considering that the free energy of adsorbed H is the most important factor to predict the activity of HER, most of DFT predictions will be invalid if equation is incorrect.

Response: Thank you for your careful check and suggestion. The free energy is calculated using the equation $G = E + \text{ZPE} - TS$. To avoid output errors caused by script processing, we performed a recalculation of all atoms exposed at the top layer of HEAMs. In the revised version, we utilized Vaspkit software to individually output results instead of batch processing the data, resulting in consistent calculation results with the original trend change. The updated calculation results are presented in the question 2.

Supplementary Table 5. Adsorption energy of H species (ΔE_{H^*}), the relevant contributions to the free energy (ΔZPE and $T\Delta S$), and the free energy of adsorbed H* (ΔG_{H^*}) on different sites on the surfaces of HEMs.

ΔG_{H^*} (eV)	ΔE_{H^*} (eV)	ΔZPE (eV)	$T\Delta S$ (eV)	Site
-0.615	-0.760178	0.157852	0.012674	Fe1 top
-0.642	-0.783684	0.157655	0.015971	Mn1 top
-0.242	-0.373501	0.145014	0.013513	Pd1 top
-0.238	-0.36369	0.142526	0.016836	Pd2 top
-0.272	-0.406013	0.149499	0.015486	Pd3 top
-0.682	-0.815997	0.151355	0.017357	Mn2 top
-0.682	-0.809863	0.143828	0.015965	Mn3 top
-0.687	-0.825537	0.153059	0.014522	Mn4 top
-0.436	-0.574556	0.153052	0.014496	Fe2 top
-0.132	-0.256948	0.140729	0.015781	Rh1 top
-0.242	-0.376385	0.148027	0.013642	Pd4 top
-0.425	-0.570145	0.157793	0.012648	Fe3 top
-0.145	-0.285793	0.156215	0.015422	Rh2 top
-0.23	-0.360034	0.143693	0.013659	Pd5 top
-0.524	-0.667479	0.157513	0.014034	Mo1 top
-0.557	-0.700467	0.157501	0.014034	Mo2 top
-0.782	-0.891416	0.123952	0.014536	Mn1Mn2 bridge1
-0.782	-0.914873	0.148336	0.015463	Mn1Mn3 bridge2
-0.782	-0.92433	0.157793	0.015463	Mn2Mn3 bridge3
-0.782	-0.925568	0.157793	0.014224	Mn3Mn4 bridge4
-0.29	-0.421217	0.145145	0.013928	Pd1Pd2 bridge1
-0.546	-0.679138	0.146852	0.013714	Mo1Mo2 bridge1
-0.674	-0.816518	0.156215	0.013697	Mn1-Mn2- Mn3 Holllow

Supplementary Table 6. Adsorption energy of H species (ΔE_{H^*}), the relevant contributions to the free energy (ΔZPE and $T\Delta S$), and the free energy of adsorbed H* (ΔG_{H^*}) on Rh or Pd sites over PdRh, PdMoFeMn, RhMoFeMn, and HEMs.

Species	ΔE_{H^*} (eV)	ΔZPE (eV)	$-T\Delta S$ (eV)	ΔG_{H^*} (eV)
H ₂		0.287212	0.410024	
H* on Rh site of HEMs	-0.256948	0.140729	0.015781	-0.132
H* on Rh site of RhMoFeMn	-0.596889	0.147255	0.015366	-0.465
H* on Rh site of PdRh	-0.537682	0.154264	0.144582	-0.528

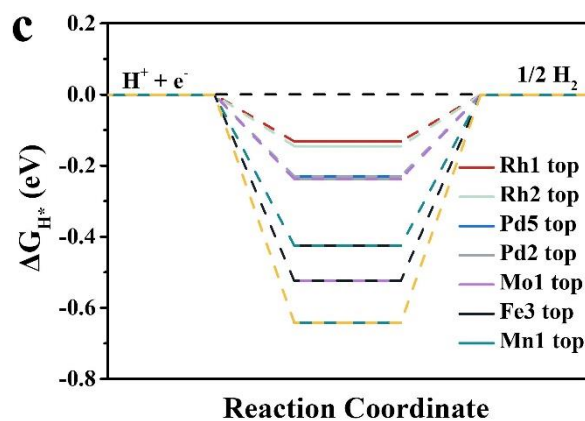
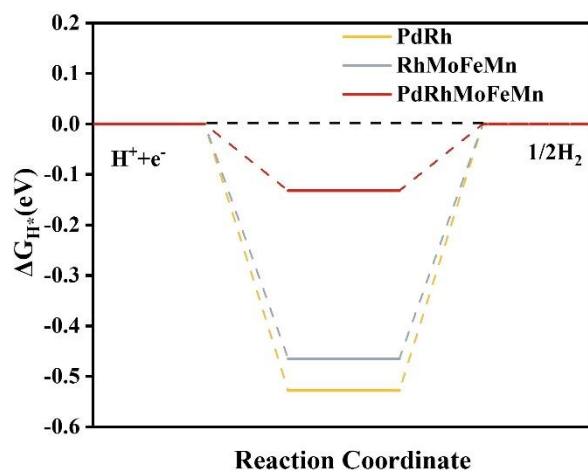


Fig. 5c The ΔG_{H^*} profiles on various catalytic sites of PdRhMoFeMn HEMs.



Supplementary Fig. 34 The adsorption energies of H_{ads} on PdRh, PdMoFeMn, RhMoFeMn, and PdRhMoFeMn.

Changes to the main text:

Line 346: Fig. 5c reveals that the Rh top site has the lowest ΔG_{H^*} (-0.132 eV) relative to other comparison sites, indicating that the Rh site has the best binding strength to hydrogen and serves as the main active ingredient to contribute the excellent acidic HER performance.

Line 351: As displayed in Supplementary Fig. 34 and Supplementary Table 6, The ΔG_{H^*} of PdRhMoFeMn is -0.132 eV, significantly higher than -0.528 eV of PdRh and -0.465 eV of RhMoFeMn.

Q3. In computational method, the DFT + U method was adopted in this work. Generally, the DFT + U is used to correct the energy for the system with strongly correlated electrons or localized electrons, like many metal oxide system. As for the metal or alloy system, it is not necessary to introduce DFT + U. Please explain why adopting DFT + U method in this work to model high-entropy metallenes.

Response: Thanks for your question. In the investigation of alloys or compounds involving 3d, 4d, and 5d transition metals, as well as lanthanide rare earth elements, the strong correlation properties exhibited by their d or f electrons can sometimes lead to inaccuracies in traditional Density Functional Theory (DFT) calculations, particularly when employing the Local Density Approximation (LDA) or Generalized Gradient Approximation (GGA). These inaccuracies are especially pronounced in predicting band gaps. Furthermore, it should be noted that the Kohn-Sham orbitals utilized in DFT are not true atomic orbitals, resulting in pseudo-band gap calculations. To address these challenges effectively albeit at a higher computational cost, hybrid functionals or Hartree-Fock methods can be employed. The incorporation of corrections for strong correlation effects through the DFT+U method offers a viable solution within GGA+U and LDA+U frameworks.

Q4. In 321st line of the manuscript, the authors mentioned that the ‘Bader charge value of xx is xx’. The output of bader charge analysis is a table showing the number of electrons for each atom and this result mainly exhibits the electronic transfer/interaction in system. Therefore, the reviewer is confused about the definition of ‘bader charge value’ and please provide how to calculate the bader charge value. Moreover, please explain why a higher bader charge value represents a higher

electrical conductivity.

Response: We apologize for any confusion caused. The calculation steps for Bader charge are present at the end of this question. In our computation of Bader charge, we summed the charges from all atoms in the models (PdRh, PdRhMoFeMn, RhMoFeMn), which might have led to the confusion. Generally, differences in charge between atoms can induce electron transfer and rearrangement, altering the charge distribution. However, comparing these differences across our three models (PdRh, PdRhMoFeMn, RhMoFeMn) is somewhat inappropriate due to their significant structural variations. Such comparisons are more suitable for studies involving deficient or doped catalysts. Therefore, after discussion, we decided to omit this part of the content.

Steps:

1. Relax the system to a converged geometry.
2. Using the relaxed geometry, perform static calculation using the following tags:
LAECHG=.TRUE.
3. Sum the output charge files AECCAR0 AECCAR2 using the the chgsum.pl script.
Output the sum to CHGCAR file.
4. Run the Bader charge analysis to CHGCAR output from step#3.
5. Check if converged and vary NGX, NGY, NGZ accordingly (Iterate from step#2 to step#5 until convergence is achieved.)

Finally, we hope that all concerns have been addressed. Thank you very much again for your attention and kindness to improve our work.

Reviewer #3 (Remarks to the Author):

This manuscript shows a chemical synthesis method to produce nano-meter sized high-entropy metallenes (containing PdRhMoFeMn). This material shows low overpotentials for HER in both acidic and alkaline conditions as well as high stability. This approach is similar to previously published work. For example, Zhang et al in *Electrochimica Acta* 279, pages 19-23, showed that their high entropy alloy (Ni Fe Mo Co Cr) had excellent activity under both acidic and alkaline conditions as well as high stability. Furthermore, this high entropy alloy was free of any PGM. Similarly, the work by Li et al in *Nature Communications* (article number 5437) shows how a high entropy alloy containing one PGM, PtNiFeCoCu, reaches the same HER activity as that reported in the current manuscript, again both at acidic and alkaline conditions. And very recently, the work by Kang et al, *Nature Communications*, article number 4182, showed that PtPdRhRuCu also reached similar activities for HER and stability as reported here. In conclusion, the here proposed concept to use a high entropy material, although of different composition, is not of high enough novelty that it warrants publication in *Nature Communications*.

So maybe this work, as promised by the title, provides additional insight in the role of the different elements under operando conditions through operando XAS? The answer here is: not really.

Response: Thank you for your feedback and raising the concern regarding the novelty of our study. We appreciate your attention to previously published studies in the field of high-entropy alloys (HEAs). Firstly, the overpotential of non-precious metal high-entropy nanoparticles reported by Zhang et al. under acidic and alkaline conditions is 107 and 172 mV respectively, which is still far from the reported performance of HEA containing precious metals. The PtNiFeCoCu HEA reported by Li et al showed good HER activity only under alkaline conditions, and the precious metal content of PtPdRhRuCu mesoporous nanospheres reported by Kang et al was as high as 78%. Secondly, these reported HEA electrocatalysts are nanoparticles, and there is still a lot of development space for the accurate control of HEA catalyst morphology, especially

for high-entropy two-dimensional materials. Finally, the research on the improvement of HER performance by these HEA catalysts is not deep and comprehensive enough, and there is a lack of direct experimental evidence.

HEAs with editable multiple active sites and single-atom catalysts (SACs) with near 100% utilization efficiency of metal atoms show great potential in multi-step tandem reactions or reactions requiring multifunctional catalysts. However, most of the reported HEA catalysts are mainly nanoparticles, which lack precise morphology control and high atomic utilization efficiency. SACs with fully separated active sites lack synergy between adjacent metal atoms, which limits their catalytic efficiency. Based on this, we have designed and successfully prepared subnanometer HEMs with high atomic utilization efficiency and effective synergies between metal sites. Moreover, this is a general method that can be extended to prepare senary, septenary, and octonary HEMs, which is of great significance for the development of 2D high-entropy nanomaterials. Moreover, due to the structural complexities of HEA, the identification of the active site, the understanding of the synergistic interaction between various elements and the exploration of the reaction mechanisms at different pH are relatively lacking in the real reaction process. In this study, we first used theoretical calculations and electrochemical tests to systematically analyze the active sites in PdRhMoFeMn HEMs, the synergies between the individual elements, and the different reaction mechanisms in different electrolytes. According to the theoretical and experimental results, we used operando X-ray absorption spectroscopy techniques to identify the actual active sites in PdRhMoFeMn HEMs and visually presented their dynamics and synergistic reaction mechanisms in various electrolytes during the realistic HER process, which offer vital instruction for rationally designing high-performance HEA electrocatalysts with editable multifunctional active sites for other energy conversion applications and beyond. We believe that our study provides valuable contributions for the advancement of 2D HEA, and the in-depth understanding of their structure-property relationships. We hope this clarification addresses your concerns regarding the novelty of our study.

Thanks again for your time and suggestions to further improve this manuscript. Based

on your comments, we have revised our manuscript carefully. All changes have been highlighted in the revised manuscript by formatting the text in yellow color. Detailed lists of revisions are listed below:

Q1. How quickly after setting the potential were the operando XAS spectra measured (i.e. was this done consistently and how long does it take to collect a spectrum)?

Response: Thanks for your constructive suggestion. Each spectrum was collected within a 3-minute timeframe, during which there was continuous application of the potential (i-t).

Changes to the main text:

Line 557: Each spectrum was collected within a 3-minute timeframe, during which there was continuous application of the potential (i-t).

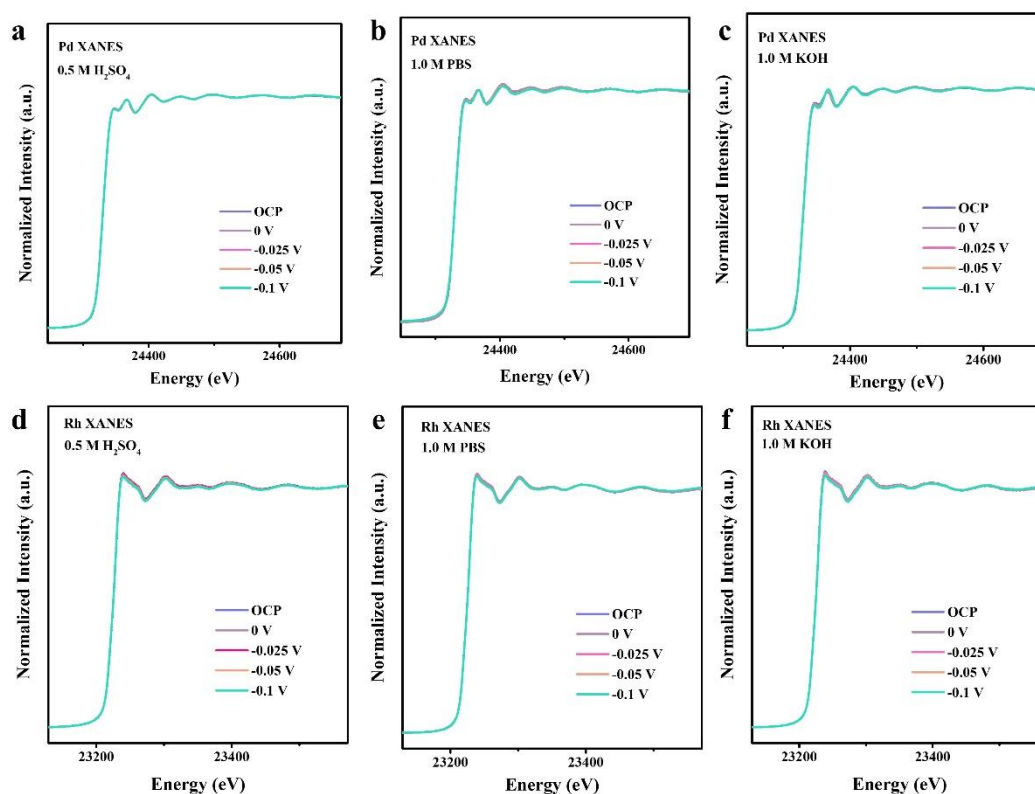
Q2. What do the Mo and Fe XANES spectra show?

Response: Thanks for your valuable suggestion. We only have Mo and Fe ex-situ XANES, and it is presented in Supplementary Fig. 5a,c. The detailed analysis is on line 172. Based on the DFT results, we tested in-situ XAS for Pd, Rh, and Mn as HER active sites. The results obtained agree with the DFT results, which also confirms our research conclusion. Due to the shortage of in-situ XAS machines, we are sorry that the in-situ XAS tests of Fe and Mo cannot be supplemented, but this does not affect our research conclusion.

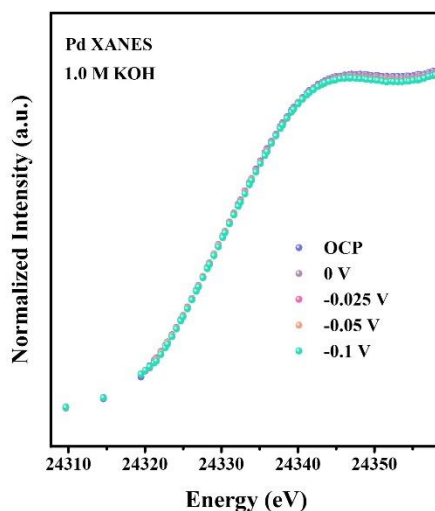
Q3. The observed shifts in the Pd and Rh XANES spectra are extremely small, and as made very clear in the pre-edge background in Figure 6e, could just be the result of non-consistent normalization. What is done to warrant absolute energy calibration? Also, what is the feature at 24319 eV in Figure c? Could it be that you have bubble formation that distorted your XANES spectra? You should have electrolyte flow in your cell to bring away bubbles.

Response: Thank you for your comments. We employed a transmission mode, and for each dataset, simultaneous measurements with metal standards were conducted. Accurate energy calibration was performed for each data as shown in the figure below, demonstrating correct normalization across a wide range of XANES spectra. As for the feature at 24319 electron volts, it is attributed to a slight irregularity caused by

differences in the number of scanning points; therefore, this feature is not a pre-edge. Given that it is around a high penetration energy of 20 KeV, the observed variation is reasonable compared to the 3d and 4d transition metals. Numerous studies have shown the sensitivity of electronic structure for Pd, Rh (Chem. Mater. 31, 15, 5663-5673 (2019); Phys. Chem. Chem. Phys. 15, 8629-8639 (2013)). We also observed the same changes in EXAFS. Hence, we consider these variations in total unoccupied states to be reasonable. The use of a transmission mode minimizes the impact of bubbles. Supplementary Figs. 44 and 46 displays prominent features over a broad spectral range.



Supplementary Fig. 44 The broad range XANES spectra of (a-c) Pd and (d-f) Rh in different electrolyte.



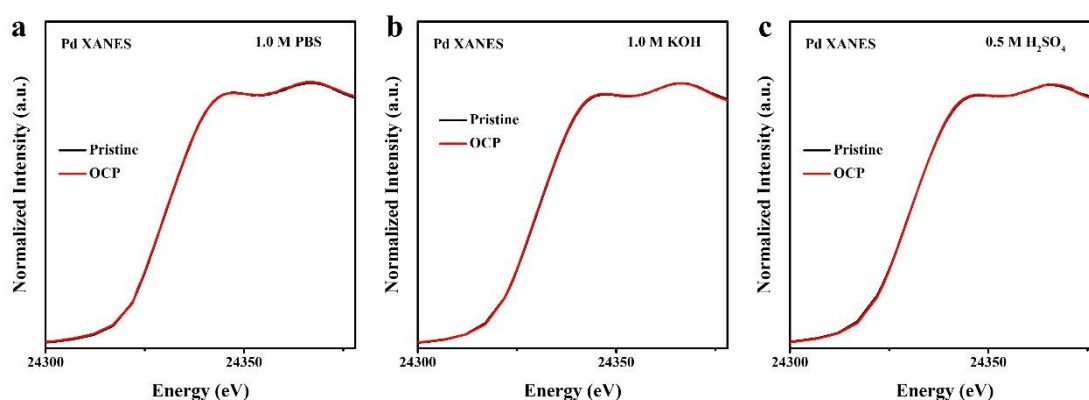
Supplementary Fig. 46 Pd scattered XANES spectra under 1.0 M KOH.

Changes to the main text:

Line 402: Supplementary Figs. 44-46 illustrates the use of scattered data to demonstrate the consistency of data processing and well-normalization across a wide range of XANES spectra.

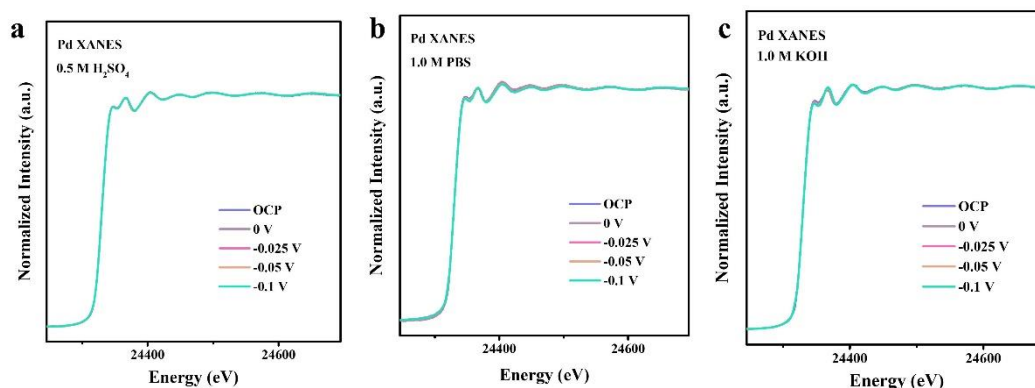
Q4. The potential reduction of the white line intensity for Pd could also be the result of a slight oxidation at higher pH, rather than an increase in electron density on the Pd atom. Please show a larger portion of your XANES spectra.

Response: Thank you for the suggestion. First, we carefully compared the pristine sample with the sample in the open circuit potential (OCP) spectra at each pH value, and found no significant differences, indicating that the changes in the data stem from the catalytic reaction (Supplementary Figs. 45). Second, the XANES spectra of Pd in a broader range have also been included (Supplementary Fig. a-c).



Supplementary Fig. 45 The Pd XANES spectra of pristine sample compared to

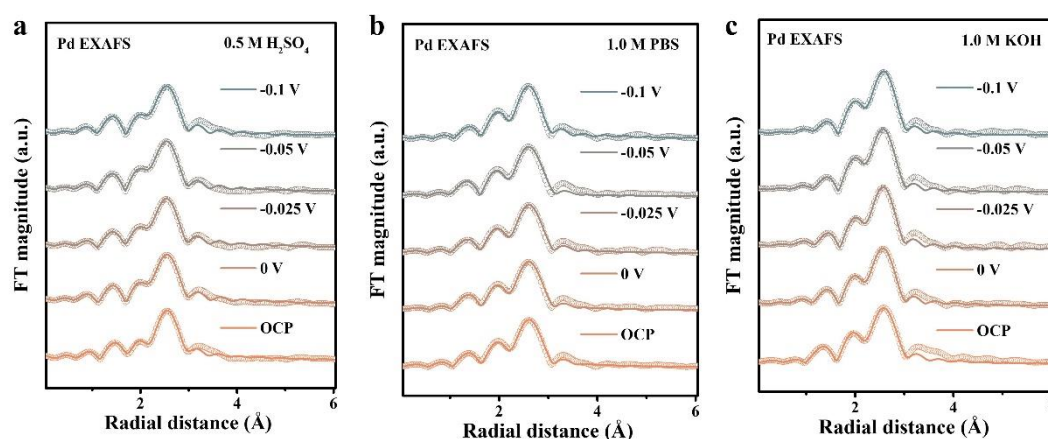
OCP state under (a) 1.0 M PBS, (b) 1.0 M KOH and (c) 0.5 M H₂SO₄ electrolyte conditions.



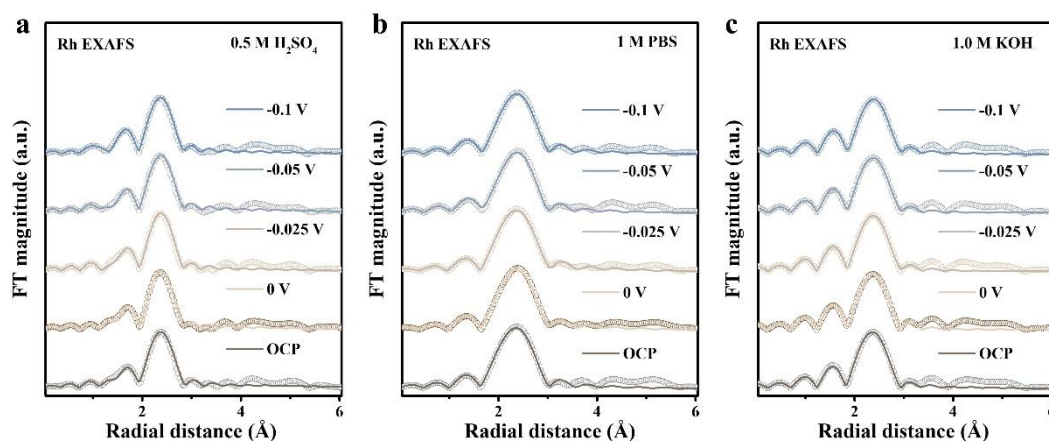
Supplementary Fig. 44 (a-c) the broad XANES spectra of Pd in different electrolyte.

Q5. Figure 7 suggests significant Pd-Pd and Rh-Rh scattering, suggesting that you do not form homogeneous metallenes.

Response: According to the important suggestions from the reviewers, we have conducted EXAFS fitting for the Rh and Pd EXAFS spectra under different electrolyte conditions (Supplementary Figs. 49 and 50, and Supplementary Tables 7-12). Additionally, we have supplemented the revised manuscript with information on Pd-M and Rh-M (M=Pd/Rh/Mo/Fe/Mn), indicating the formation of high-entropy alloys. The revised manuscript thoroughly addresses the corrections for Pd-M and Rh-M in Fig. 7.



Supplementary Fig. 49 Operando Pd EXAFS spectra of (a) 1.0 M KOH, (b) 1.0 M PBS and (c) 0.5 M H₂SO₄. The detailed fitting results are listed in Supplementary Tables 7-9.



Supplementary Fig. 50 Operando Rh EXAFS spectra of (a) 1.0 M KOH, (b) 1.0 M PBS, and (c) 0.5 M H₂SO₄. The detailed fitting results are listed in Supplementary Tables 10-12.

Changes to the main text:

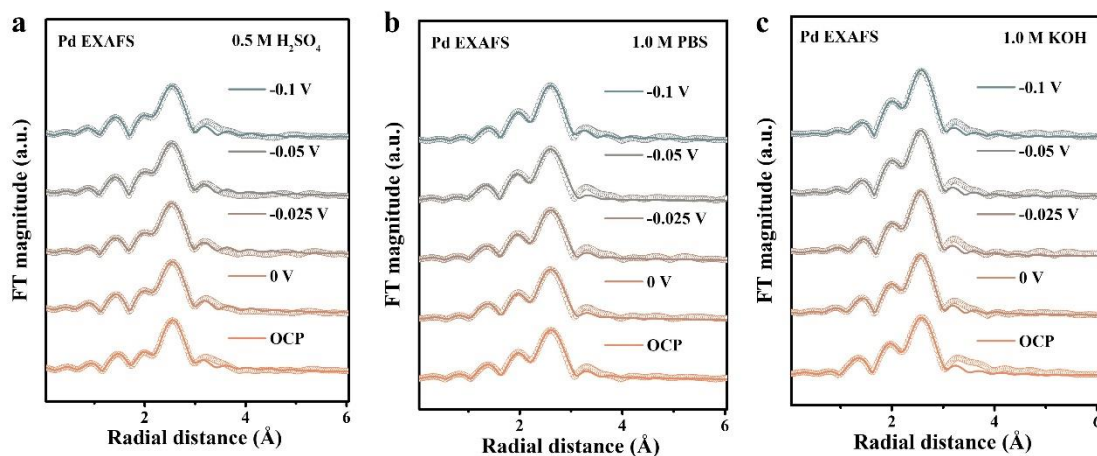
Line 521: ATHENA was used to process the acquired EXAFS data. EXAFS fitting was performed using the ARTEMIS module of the IFEFFIT and USTCXAFS software packages, and the details are presented in the Supplementary Information.

Line 451: EXAFS fitting was performed on the Rh and Pd EXAFS spectra under different electrolyte conditions (Supplementary Figs. 49 and 50, and Supplementary Tables 7-12). Additionally, we clarified the variations of Pd-M and Rh-M under operando condition, indicating the formation of high-entropy alloys.

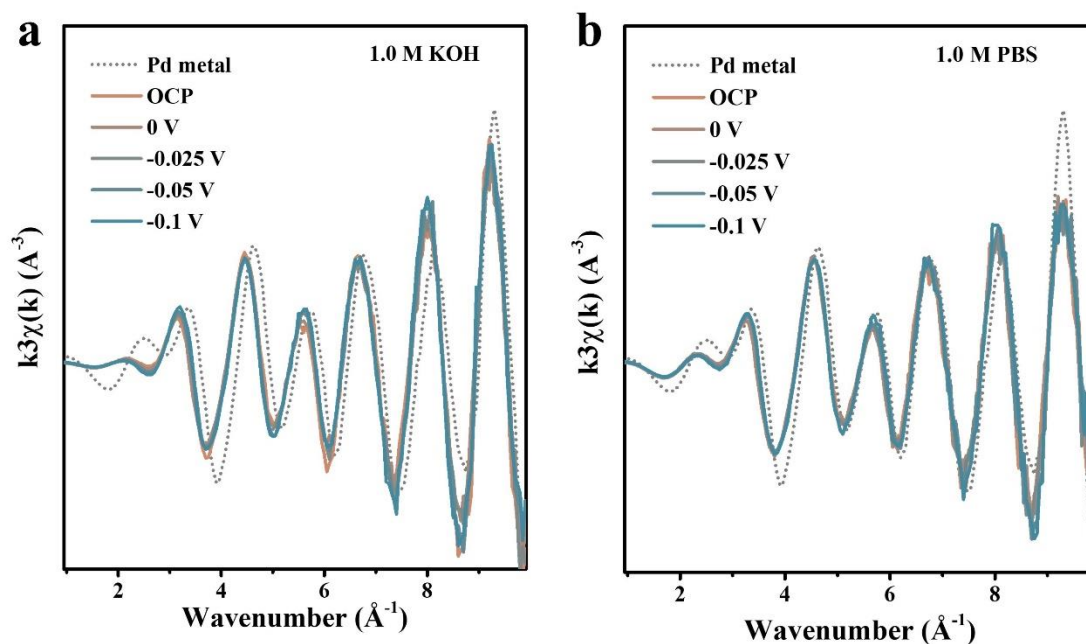
Q6. Also in Figure 7 c and e there is a significant increase in the Pd K-edge XAFS background observed (suggesting quite different noise levels) which then also leads to an increase in intensity of spectral features that you assign to Pd-O. Are spectra collected and treated consistently? Please show the k-space EXAFS spectra as well. Based on what do you assign oxygen contributions to the Pd K-XAS spectra? Did you attempt to fit the spectra?

Response: Thank you for your detailed review. In the EXAFS spectra (Supplementary Fig. 49), it can be clearly established that the data collection and processing were carried out consistently. We also present the K-space spectra, where between 3-6 Å, a slight contribution from Pd-O showing from the reaction in the electrolyte can be observed compared to reference Pd metal. The differences are

evident, and further fitting reveals the trend of Pd-O changes (Supplementary Fig. 51 and Supplementary Tables 7-9), providing evidence for the involvement of Pd in the hydrolysis process.



Supplementary Fig. 49 Operando Pd EXAFS spectra of (a) 1.0 M KOH, (b) 1.0 M PBS and (c) 0.5 M H₂SO₄. The detailed fitting results are listed in Supplementary Tables 7-9.



Supplementary Fig. 51 The corresponding $k^3\chi(k)$ oscillation functions for Pd under 1.0 M KOH and 1.0 M PBS.

Changes to the main text:

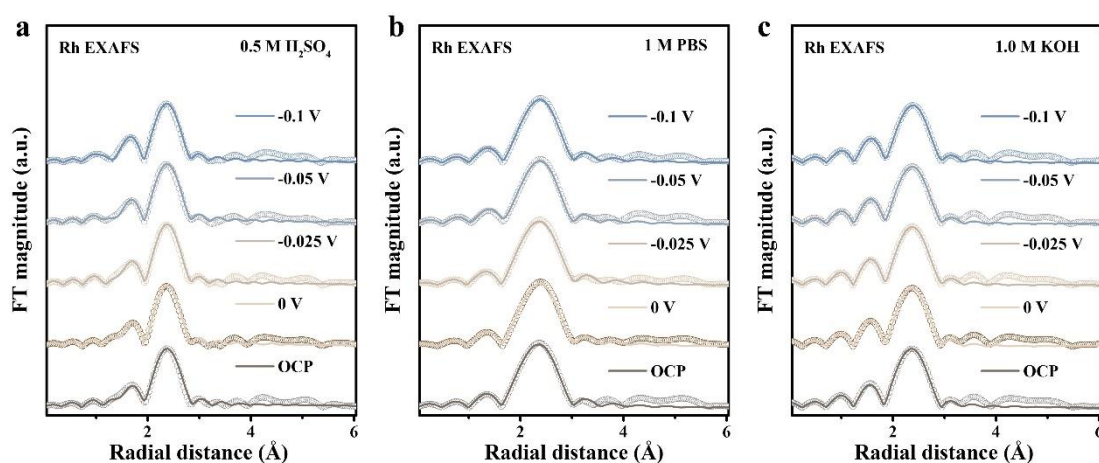
Line 447: Furthermore, Figure 7g shows an increased Pd-M peak, suggesting under both neutral and alkaline conditions, the high electron density at Pd sites is conducive

to accelerating the Volmer step, facilitating the adsorption of water and subsequent desorption of intermediate OH* species.

Line 455: Simultaneously, based on Fig S K-space spectra, where a slight contribution from Pd-O is observed between 3-6 Å, indicating the trend of water dissociation, Pd-O fitting was also conducted to further understand the dissociation of water.

Q7. Can you please explain the lower intensity between 1 and 2 Å in figure 7f vs 7 b and d? Could it be that you have an oxygen contribution there? Without fitting your EXAFS spectra, the assignments made and the discussion of the results is very speculative.

Response: Thank you for the suggestion. We have performed fitting on all Rh EXAFS spectra, and the fitting results primarily indicate the presence of highly mixed metal sites. The slight contribution in the range of 1-2 Å at the beginning is attributed to the oxygen contribution of electrolyte, and this contribution remains unchanged under various electrolyte conditions.



Supplementary Fig. 50 Operando Rh EXAFS spectra of (a) 1.0 M KOH, (b) 1.0 M PBS, and (c) 0.5 M H₂SO₄. The detailed fitting results are listed in Supplementary Tables 10-12.

Q8. DFT calculations assume a perfectly mixed alloy, but there is no proof that this is actually the case. Rather do your operando EXAFS results with a Rh-Rh and Pd-Pd scattering peak (see operando XAS results) suggest that there is local cluster formation in your materials. In contrast though, your ex-situ characterization suggests that you have a mixture of nearest neighbours. Did you attempt to fit your EXAFS

spectra? What about the many vacancies in the structure, observed by TEM, but not taken into account in the calculations?

Response: We have conducted EXAFS fitting for the Rh and Pd EXAFS spectra under different electrolyte conditions (Supplementary Figs. 49 and 50, and Supplementary Tables 7-12), indicating the formation of actually perfectly mixed alloy. Moreover, HRTEM, ACTEM, XRD, and EDS elemental mapping results also demonstrate the formation of HEAs without separated phases and clusters. Lattice distortion caused by the disordered distribution of atoms with different sizes, masses and electronegativity in equivalent positions is a basic feature of high entropy structures. For theoretical calculation, it is very difficult to build a model by taking all the factors into account, which is similar to the construction of the reported HEAs models (Nat. Commun. 13, 2662 (2022); Nat Commun 12, 6261 (2021)). This also has little impact on the purpose of using DFT to identify the role of different elements in this material in different electrolytes of HER.

Q9. The role of Rh, Pd and Mn at various pH conditions has been made clear, mostly by electrocatalytic tests. However, the role of Mo and Fe is not obvious. Why are these elements needed?

Response: We sincerely thank the reviewer for this important comment. According to the reported literature, Fe and Mo are commonly used elements to effectively reduce e_g-t_{2g} and regulate the electronic structure of the active center, which can enhance the electron transport characteristics and weaken the H adsorption energy, thereby enhancing the HER performance of noble metal alloy catalysts (Energy Environ. Sci. 16, 4009-4019 (2023); Nat Commun 13, 5497 (2022); J. Am. Chem. Soc. 144, 44, 20298–20305 (2022); Adv. Mater. 35, 2303030 (2023)). Similar results are obtained and described in line 367. Moreover, Fe and Mo have similar atomic radius to Pd, Rh, and Mn, which is more favorable for the formation of highly stable HEMs. Therefore, we selected Fe and Mo elements to enhance the structural stability and corrosion resistance of PdRhMoFeMn HEMs and optimize its electronic structure to improve its HER performance.

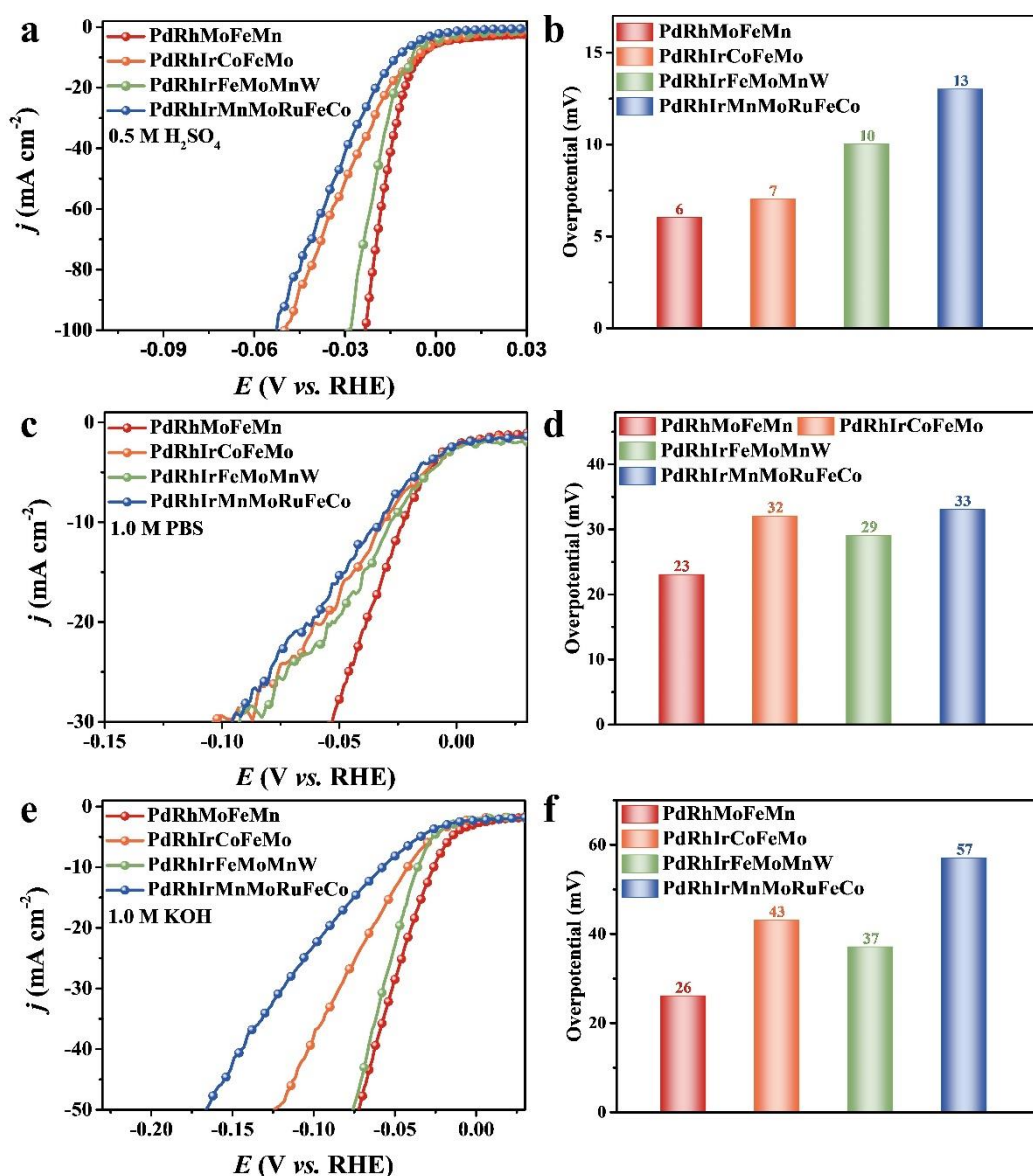
Changes to the main text:

Line 391: Moreover, Fe and Mo have similar atomic radius to Pd, Rh, and Mn, which is more favorable for the formation of highly stable HEMs.

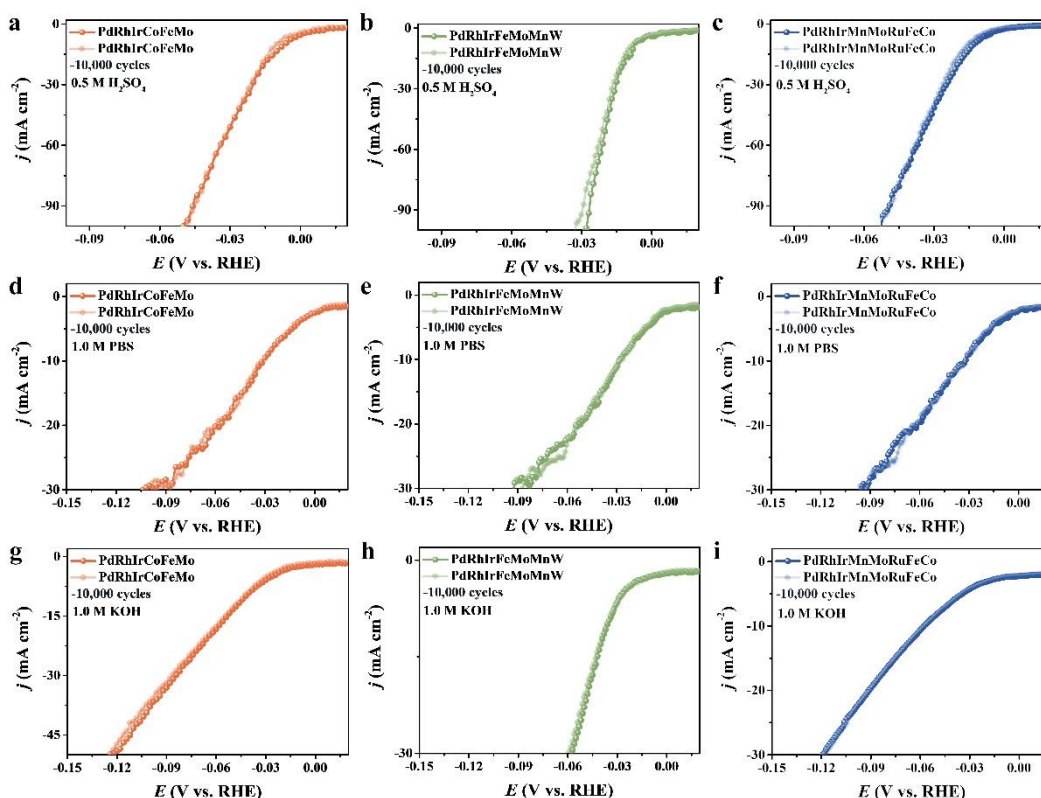
Minor comments:

Q10. You have also prepared materials containing even more elements, including Ir. Why were there materials not tested and characterized for HER?

Response: Thank the reviewer for the helpful suggestion. We prepared senary PdRhIrCoFeMo, septenary PdRhIrFeMoMnW, and octonary PdRhIrMnMoRuFeCo HEMs to demonstrate the universality of this synthesis approach, which can be used to synthesize other high-entropy two-dimensional materials with editable active sites for other energy conversion applications and beyond. We also added HER performance tests for these HEMs and compared them with PdRhMoFeMn HEMs. As shown in Supplementary Fig. 27, quinary PdRhMoFeMn HEMs exhibit the low η_{10} values of 6, 23 and 26 mV, superior to senary PdRhIrCoFeMo HEMs (7, 32 and 43 mV), septenary PdRhIrFeMoMnW HEMs (10, 29 and 37 mV), and octonary PdRhIrMnMoRuFeCo HEMs (13, 33 and 57 mV) in 0.5 M H₂SO₄, 1.0 M PBS, and 1.0 M KOH electrolytes, respectively. The reasons for the higher activity of quinary HEMs are as follows: First, the thickness of quinary HEMs is only about 1.0 nm, which is thinner than that of senary (1.33 nm), septenary (1.40 nm) and octonary (1.46 nm) HEMs, indicating more exposed active sites and higher atomic utilization efficiency. Furthermore, Rh and Pd active components that are highly effective for HER have higher content in quinary HEMs compared to other HEMs. All these HEMs exhibit small negative shifts after 10,000 CV cycles, indicating their excellent electrochemical stability (Supplementary Fig. 28).



Supplementary Fig. 27 Electrocatalytic HER performance evaluation of quinary PdRhMoFeMn, senary PdRhIrCoFeMo, septenary PdRhIrFeMoMnW, and octonary PdRhIrMnMoRuFeCo HEMs. (a) Polarization curves and (b) corresponding overpotentials at 10 mA cm⁻² of HEMs with different composition in 0.5 M H₂SO₄. (c) Polarization curves and (d) corresponding overpotentials at 10 mA cm⁻² of HEMs with different composition in 1.0 M PBS. (e) Polarization curves and (f) corresponding overpotentials at 10 mA cm⁻² of HEMs with different composition in 1.0 M KOH.



Supplementary Fig. 28 Electrochemical HER stability tests of senary PdRhIrCoFeMo, septenary PdRhIrFeMoMnW, and octonary PdRhIrMnMoRuFeCo HEMs. The polarization curves of (a) senary HEMs, (b) septenary HEMs, and (c) octonary HEMs before and after 10,000 CV cycles in 0.5 M H₂SO₄. The polarization curves of (d) senary HEMs, (e) septenary HEMs, and (f) octonary HEMs before and after 10,000 CV cycles in 1.0 M PBS. The polarization curves of (g) senary HEMs, (h) septenary HEMs, and (i) octonary HEMs before and after 10,000 CV cycles in 1.0 M KOH.

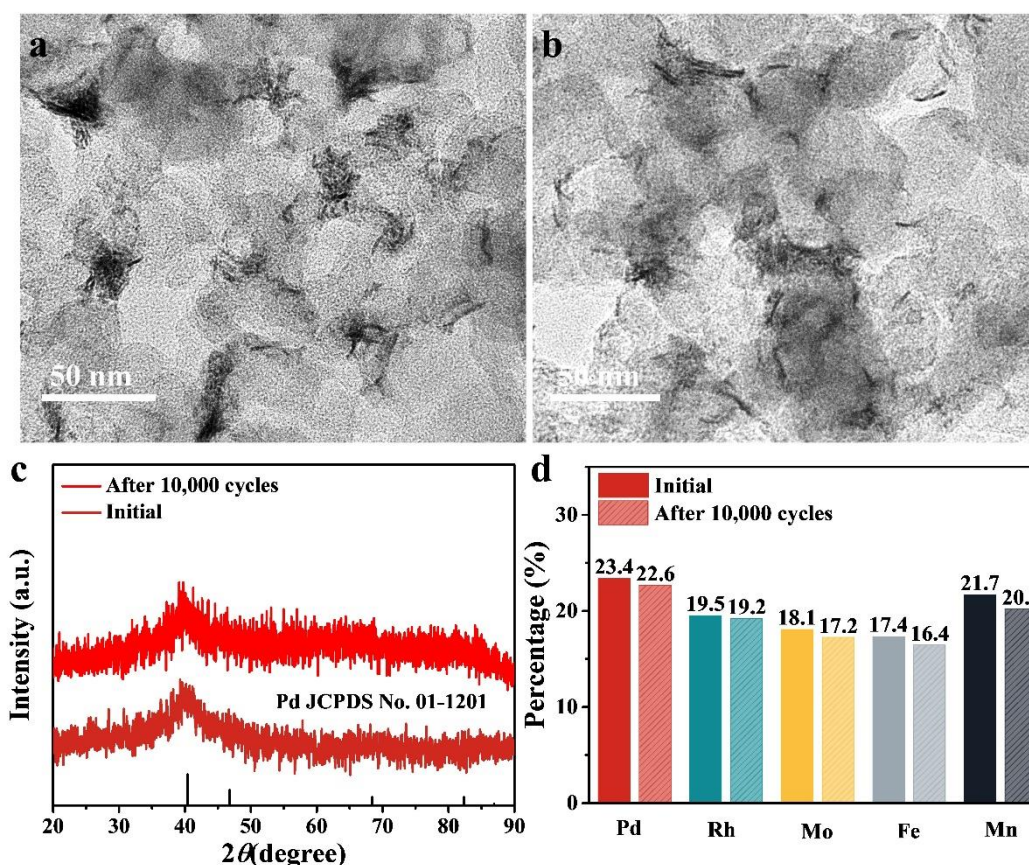
Changes to the main text:

Line 320: Additionally, the HER performance of quinary PdRhMoFeMn HEMs were also compared with that of senary PdRhIrCoFeMo, septenary PdRhIrFeMoMnW, and octonary PdRhIrMnMoRuFeCo HEMs. As shown in Supplementary Fig. 27, PdRhMoFeMn HEMs exhibit smaller overpotential than senary, septenary, and octonary HEMs at the same current density under acidic, neutral, and alkaline environments due to better atomic utilization efficiency and active site configurations. Particularly, all these HEMs exhibit small negative shifts after 10,000 CV cycles,

indicating their excellent electrochemical stability (Supplementary Fig. 28).

Q11. Stability tests have been made to show that the material is quite stable. Can you please provide the same physical chemical characterization of the PdRhMoFeMn material after the stability tests? i.e., are all elements stable, or do some elements preferentially leach out? Also, there is a large discrepancy in the elemental analysis by SEM-EDS and ICP-OES for Rh, please address this.

Response: Thanks for your valuable suggestion. According to your comments, we have supplemented TEM, XRD, and ICP-OES tests before and after stability to explore the reasons for its high stability. As shown in Supplementary Fig. 18a,b, the morphology of nanosheet was well maintained. The catalyst is still well dispersed on the carbon and there is no significant aggregation. XRD and ICP-OES results indicate that the crystal structure and composition of PdRhMoFeMn HEMs have not changed obviously, further suggesting their robustness (Supplementary Fig. 18c,d). In addition, the reason for the big difference between the elemental analysis results of SEM-EDS and ICP-OES for Rh is that we used aqua regia to dissolve the sample, and Rh is more stable in strong acid solution than the other elements, which leads to its lower content tested by ICP-OES. We have sent the samples to a professional ICP-OES company for re-testing. They used microwave digestion to dissolve the samples, so that the content of Rh was more accurate and closer to SEM-EDS results.



Supplementary Fig. 18 Characterizations of PdRhMoFeMn HEMs before and after 10,000 CV cycles. TEM images (a) before and (b) after 10,000 CV cycles. (c) XRD pattern before and after 10,000 CV cycles. (d) ICP-OES results before and after 10,000 CV cycles.

Changes to the main text:

Line 260: Besides, the TEM images show that PdRhMoFeMn HEMs maintain the nanosheet shape and the distribution on the carbon is still uniform without aggregation (Supplementary Fig. 18a,b). XRD results in Supplementary Fig. 18c suggest that (111) facet-dominated fcc structure could be well retained after 10,000 cycles. Moreover, the ICP-OES characterizations before and after 10,000 cycles further indicate that there was no obvious change in the composition of PdRhMoFeMn HEMs, further suggesting their robustness (Supplementary Fig. 18d).

Line 134: The Pd/Rh/Mo/Fe/Mn ratio was determined by the SEM energy dispersive X-ray spectroscopy (SEM-EDS) to be 23.52/20.97/17.42/16.58/21.51 (Fig. 2e). Similar results were obtained from the inductively coupled plasma optical emission spectroscopy (ICP-OES) measurement

(Pd/Rh/Mo/Fe/Mn=23.37/19.53/18.07/17.35/21.68) (Supplementary Table 1).

Q12. Lines 351-355: There is a disconnect between your experimental data, which suggest Pd is the active site at higher pH and the DFT calculations (the delta G descriptor) that suggests Rh is the active site over the whole pH range. How much stock should we put in these DFT calculations (and what is the relevance of thermal stability calculations)?

Response: Thanks for your valuable comments. Both theoretical and experimental results show that the Rh site serves as the only active center for the stepped-up coupling of H* to H₂ in acidic electrolytes. In alkaline and neutral solutions, Rh is still the adsorption and coupling site of H, while Pd is the adsorption and dissociation site of water. Therefore, Rh is the active site for adsorption and coupling of H in all pH ranges. The difference is that due to the hydrolytic dissociation step under alkaline and neutral, this occurs on additional Pd active centers. The theoretical and experimental results are consistent. In our model, we have constructed a four-layered atomic structure with a total layer spacing of approximately 8 Å (angstroms) from top to bottom of PdRhMoFeMn. Generally, the impact on electronic properties is negligible when the distance between atoms exceeds 10 angstroms. To assess its stability, molecular dynamics simulations at various temperatures (Fig. 5b) were conducted and demonstrated that HEMs exhibit excellent stability.

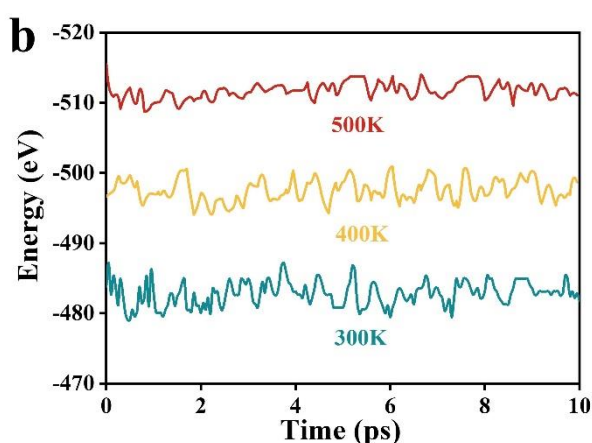


Figure 5b Molecular dynamics simulations of PdRhMoFeMn HEMs at 300, 400, and 500 K.

Finally, we hope that all concerns have been addressed. Thank you very much again for your attention and kindness to improve our work.

Supplementary Table 7. Model-fitted operando EXAFS spectra results for Pd under KOH.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Pd-O	0.169	2.127	0.00401	-5.000	0.00447
	Pd-Pd/Rh	1.433	2.666	0.00701	1.759	
	Pd-Mo	3.688	2.818	0.00701	0.603	
	Pd-Fe/Mn	1.000	2.939	0.00701	8.312	
0 V	Pd-O	0.410	2.127	0.00401	-5.000	0.00301
	Pd-Pd/Rh	1.433	2.562	0.00701	0.715	
	Pd-Mo	3.688	2.782	0.00701	0.241	
	Pd-Fe/Mn	1.108	2.965	0.00701	8.312	
-0.025 V	Pd-O	0.531	2.127	0.00401	-5.000	0.00691
	Pd-Pd/Rh	1.433	2.561	0.00701	6.584	
	Pd-Mo	3.688	2.783	0.00701	0.069	
	Pd-Fe/Mn	1.320	2.967	0.00701	8.312	
-0.05 V	Pd-O	0.643	2.127	0.00401	-5.000	0.00470
	Pd-Pd/Rh	1.433	2.659	0.00701	3.020	
	Pd-Mo	3.688	2.819	0.00701	0.246	
	Pd-Fe/Mn	1.391	2.910	0.00701	8.312	
-0.1 V	Pd-O	0.665	2.127	0.00401	-5.000	0.00486
	Pd-Pd/Rh	1.433	2.689	0.00701	3.389	
	Pd-Mo	3.688	2.828	0.00701	0.987	
	Pd-Fe/Mn	1.417	2.936	0.00701	8.312	

Supplementary Table 8. Model-fitted operando EXAFS spectra results for Pd PBS.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Pd-O	0.163	2.127	0.00401	-5.000	0.00376
	Pd-Pd/Rh	1.433	2.674	0.00701	7.164	
	Pd-Mo	3.688	2.824	0.00701	4.016	
	Pd-Fe/Mn	1.002	2.897	0.00701	8.411	
0 V	Pd-O	0.167	2.127	0.00401	-5.000	0.00431
	Pd-Pd/Rh	1.433	2.666	0.00701	7.771	
	Pd-Mo	3.688	2.824	0.00701	4.219	
	Pd-Fe/Mn	1.081	2.915	0.00701	8.410	
-0.025 V	Pd-O	0.176	2.127	0.00401	-5.000	0.00351
	Pd-Pd/Rh	1.433	2.666	0.00701	7.370	
	Pd-Mo	3.688	2.823	0.00701	4.288	
	Pd-Fe/Mn	1.142	2.904	0.00701	8.416	
-0.05 V	Pd-O	0.241	2.127	0.00401	-5.000	0.00617
	Pd-Pd/Rh	1.433	2.668	0.00701	9.140	
	Pd-Mo	3.688	2.830	0.00701	5.010	
	Pd-Fe/Mn	1.434	2.920	0.00701	8.416	
-0.1 V	Pd-O	0.251	2.127	0.00401	-5.000	0.00359
	Pd-Pd/Rh	1.433	2.688	0.00701	6.615	
	Pd-Mo	3.688	2.813	0.00701	1.874	
	Pd-Fe/Mn	1.532	2.892	0.00701	8.416	

Supplementary Table 9. Model-fitted operando EXAFS spectra results for Pd under H₂SO₄.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Pd-O	0.171	2.127	0.00401	-5.000	0.00395
	Pd-Pd/Rh	1.433	2.658	0.00701	-6.355	
	Pd-Mo	3.688	2.774	0.00701	-3.175	
	Pd-Fe/Mn	1.000	2.965	0.00701	8.312	
0 V	Pd-O	0.171	2.127	0.00401	-5.000	0.00296
	Pd-Pd/Rh	1.433	2.658	0.00701	-8.211	
	Pd-Mo	3.688	2.819	0.00701	-1.740	
	Pd-Fe/Mn	1.000	2.870	0.00701	8.312	
-0.025 V	Pd-O	0.171	2.127	0.00401	-5.000	0.00203
	Pd-Pd/Rh	1.433	2.638	0.00701	-11.225	
	Pd-Mo	3.688	2.812	0.00701	-0.953	
	Pd-Fe/Mn	1.000	2.839	0.00701	8.125	
-0.05 V	Pd-O	0.171	2.127	0.00401	-5.000	0.00163
	Pd-Pd/Rh	1.433	2.653	0.00701	-10.765	
	Pd-Mo	3.688	2.783	0.00701	0.298	
	Pd-Fe/Mn	1.000	2.967	0.00701	12.665	
-0.1 V	Pd-O	0.171	2.127	0.00401	-5.000	0.0446
	Pd-Pd/Rh	1.433	2.555	0.00701	-8.406	
	Pd-Mo	3.688	2.823	0.00701	-1.921	
	Pd-Fe/Mn	1.000	2.893	0.00701	8.312	

Supplementary Table 10. Model-fitted operando EXAFS spectra results for Rh under KOH.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Rh-O	0.247	1.881	0.00623	0.000	0.00181
	Rh-Rh/Pd	2.149	2.532	0.00712	2.172	
	Rh-Mo	4.830	2.714	0.00712	6.857	
	Rh-Fe/Mn	2.302	2.609	0.00712	8.776	
0 V	Rh-O	0.247	1.881	0.00623	0.000	0.00177
	Rh-Rh/Pd	2.149	2.532	0.00712	2.726	
	Rh-Mo	4.830	2.714	0.00712	7.413	
	Rh-Fe/Mn	2.302	2.609	0.00712	8.776	
-0.025 V	Rh-O	0.247	1.881	0.00623	0.000	0.00146
	Rh-Rh/Pd	2.149	2.523	0.00712	3.179	
	Rh-Mo	4.830	2.714	0.00712	7.614	
	Rh-Fe/Mn	2.302	2.607	0.00712	8.776	
-0.05 V	Rh-O	0.247	1.881	0.00623	0.000	0.00182
	Rh-Rh/Pd	2.149	2.523	0.00712	2.680	
	Rh-Mo	4.830	2.714	0.00712	7.380	
	Rh-Fe/Mn	2.302	2.610	0.00712	8.776	
-0.1 V	Rh-O	0.247	1.881	0.00623	0.000	0.00173
	Rh-Rh/Pd	2.149	2.523	0.00712	2.781	
	Rh-Mo	4.830	2.714	0.00712	7.556	
	Rh-Fe/Mn	2.302	2.610	0.00712	8.776	

Supplementary Table 11. Model-fitted operando EXAFS spectra results for Rh under PBS.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Rh-O	0.127	1.881	0.00521	0.000	0.00169
	Rh-Rh/Pd	2.149	2.551	0.00712	-10.369	
	Rh-Mo	4.830	2.737	0.00712	7.939	
	Rh-Fe/Mn	2.302	2.602	0.00712	-0.511	
0 V	Rh-O	0.127	1.881	0.00521	0.000	0.00214
	Rh-Rh/Pd	2.149	2.554	0.00712	-8.682	
	Rh-Mo	4.830	2.740	0.00712	8.675	
	Rh-Fe/Mn	2.302	2.602	0.00712	0.442	
-0.025 V	Rh-O	0.127	1.881	0.00521	0.000	0.00166
	Rh-Rh/Pd	2.149	2.563	0.00712	-9.349	
	Rh-Mo	4.830	2.740	0.00712	8.605	
	Rh-Fe/Mn	2.302	2.602	0.00712	-1.556	
-0.05 V	Rh-O	0.127	1.881	0.00521	0.000	0.00180
	Rh-Rh/Pd	2.149	2.545	0.00712	-6.711	
	Rh-Mo	4.830	2.740	0.00712	8.907	
	Rh-Fe/Mn	2.302	2.602	0.00712	3.812	
-0.1 V	Rh-O	0.127	1.881	0.00521	0.000	0.00104
	Rh-Rh/Pd	2.149	2.549	0.00712	-9.843	
	Rh-Mo	4.830	2.740	0.00712	8.799	
	Rh-Fe/Mn	2.302	2.602	0.00712	-0.250	

Supplementary Table 12. Model-fitted operando EXAFS spectra results for Rh under H₂SO₄.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Rh-O	0.251	1.881	0.00623	0.000	0.00518
	Rh-Rh/Pd	2.149	2.499	0.00712	-0.151	
	Rh-Mo	4.830	2.691	0.00712	4.700	
	Rh-Fe/Mn	2.302	2.621	0.00712	10.398	
0 V	Rh-O	0.251	1.881	0.00623	0.000	0.00572
	Rh-Rh/Pd	2.149	2.499	0.00712	-0.606	
	Rh-Mo	4.830	2.690	0.00712	4.079	
	Rh-Fe/Mn	2.302	2.621	0.00712	9.805	
-0.025 V	Rh-O	0.251	1.881	0.00623	0.000	0.00595
	Rh-Rh/Pd	2.149	2.499	0.00712	0.093	
	Rh-Mo	4.830	2.689	0.00712	4.142	
	Rh-Fe/Mn	2.302	2.621	0.00712	10.019	
-0.05 V	Rh-O	0.251	1.881	0.00623	0.000	0.00674
	Rh-Rh/Pd	2.149	2.499	0.00712	0.113	
	Rh-Mo	4.830	2.689	0.00712	3.841	
	Rh-Fe/Mn	2.302	2.621	0.00712	10.072	
-0.1 V	Rh-O	0.251	1.881	0.00623	0.000	0.00597
	Rh-Rh/Pd	2.149	2.499	0.00712	0.076	
	Rh-Mo	4.830	2.687	0.00712	3.404	
	Rh-Fe/Mn	2.302	2.621	0.00712	9.836	

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have satisfactorily addressed the reviewer's comments. The revised manuscript is acceptable for publication in this journal.

Reviewer #2 (Remarks to the Author):

In the revised manuscript, the authors addressed some comments from the reviewer. The updated results in Supplementary Table 5 are very solid now. However, the authors still had some concerns in the computational part.

1. In the computational method, the Monkhorst-Pack k-point mesh of $3 \times 2 \times 1$ was adopted in this work. However, the cell parameters of $a=b=10.58010 \text{ \AA}$, and $c=21.84430 \text{ \AA}$ were used. It is weird that a is equal to b but the k-point mesh along a and b are not equal. Please double check this computational setup.
2. In DFT part, the authors pointed out 'Rh top site has the lowest $\Delta G H^*$ (-0.132 eV) relative to other comparison sites'. However, the $\Delta G H^*$ was predicted to be more negative on other sites in Figure 5c. This result turns out that Rh site is the most active site to promote HER, but it cannot prove that hydrogen prefers to be adsorbed on Rh site. Based on Figure 5c, Pd2 site exhibits the lowest value of $\Delta G H^*$, implying that hydrogen prefers to be adsorbed on this site. If the authors want to highlight the activity enhancement of HEA, it is suggested to compare the average $\Delta G H^*$ even though it is not very accurate to evaluate the HER activity of HEA.
3. Please check the Figure 5c. The color of the solid line is not consistent with that of the dash line.
4. In Supplementary Figure 37-40, please mark the name of the structure corresponding to that in Figure 5h. Moreover, please check if H-OH is adsorbed on the surface. If so, please change it to '*H-OH' in Figure 5h.
5. In Supplementary Figure 41, the energy of 'OH +*' is much lower than of '*OH'. The reviewer is surprised by this result since the energy of isolated OH (which is a radical) should be very high. Please check this result.
6. In Supplementary Figure 42, the reviewer highlighted that the results were from NEB. The reviewer is confused about how to use NEB calculations to predict binding energy. Please provide more details about it.

Reviewer #3 (Remarks to the Author):

I have thoroughly read the revised manuscript and the reply to reviewers. In general, most of my questions have been addressed. However, while I thank the authors for now including the fits of the EXAFS spectra (this was really missing), the discussion of the fitting results and XAS data in general needs some further thoughts as the only real novelty of this manuscript is that some structure-performance relationships might be deciphered from the data.

Additional (minor) comments:

Page 4, line 77: 'challenging' in what respect?

Page 4, line 89, there is quite a bit of literature on the application of XAS to study the dynamics of bimetallic systems. Please rephrase

Fig 2d and line 216: The absence of other phases in XRD does not mean no additional phases are formed, XRD only detects crystalline phases larger as 3 nm, no amorphous phases.

Page 8, line 166: Well, the peaks are not yet corrected for phase shifts. You should refer here to your fitting results, which do indicate Rh-Rh and Pd-Pd neighbours, suggesting the presence of small clusters. Actually, the Rh-Rh distance is really close to that in foil and the Pd-Pd distance is not too far off, likely as a result of the observed distortions of the structure due to the smaller atoms present.

Reply of authors: The Pd-O and Rh-O contributions observed are direct bonds at well defined bond distances. If this was O from the electrolyte you would not observe such a well-defined bond. So, most likely these are Pd-O and Rh-O bonds directly at the surface of the HEMs as you have no further indication of oxidation of Pd and Rh (L edges are much more sensitive). However, XPS indicates surface oxide as well. Please incorporate this observation in your manuscript as the surface chemistry influences the reaction mechanism.

Line 187: why contrastively? Your (XPS and EXAFS fits) data clearly suggest that Pd and Rh are also oxidized at the surface.

Synthesis procedure: at what concentrations were the different elements initially mixed? Does that correspond to the measured ratio by ICP-OES?

Line 263: aggregation of carbon or of the HEM? Do you have the XAS spectra after 10000 cycles, this is the best probe to show local structure change? Your Mn EXAFS data (fits are missing) clearly suggest the formation of a Mn oxide, which then suggest significant structural changes within the HEM on the local scale.

Line 327: 'presumably due to better atom utilization', there is no direct proof for this.

Line 354: check grammar of this new sentence

Line 354: How does ΔG for Rh change if the coordination around Rh changes from a homogeneous HEM to one with clusters (and Mn/Fe oxide)?

Line 405: really not clear what you mean by 'scattered data' (which is only presented in Figure S46, not S44-46 as stated in the text)

Line 412: what do you mean by 'enhanced electronic intensity'? Do you mean enhanced electron density?

Line 416: how about charge transfer from Fe and Mo?

Line 417 and Figure S47 and related discussion on formation of hydroxyl groups at Mn: Not sure how to interpret this, definitely not a consistent behaviour over the pH range. A) the changes here might just be a normalization problem. The edge energy seems to be the same. B) here the overall coordination of Mn changes as well: what happens here? EXAFS suggest formation of Mn oxide, suggesting significant reordering of the HEM as a result C) this is a very small change in oxidation state, but at the same time large changes in the EXAFS suggesting the same structural reordering as in B. Forming of a significant Mn oxide is not the same as formation of OH groups on Mn. Please discuss.

Page 436: this is not an 'elevation', but an increase in peak intensity. There is more that could go in an increase in intensity as just an increase in coordination number, it could also be a decrease of the pseudo-Debye Waller factor. Here you should really go with your EXAFS fitting results. Please add this to the manuscript and discuss. Here I see a consistent fitting of Pd-O coordination numbers across the pH range.

Line 443: if you get an increase in Pd-M coordination number (please check your EXAFS fits) than that suggests significant reordering of your HEM at different pH, and thus less stability of the HEM as suggested in the manuscript.

Line 457: k-space, not with a capital. These spectra should be k^2 weighted at most.

Supplementary 413- : please give a reference to all software packages used. For example, IFEFFIT has been called the Demeter software suite for ages now. Not quite sure I understand the fitting strategy, one can not fit the coordination number and amplitude reduction factor simultaneously. Please report the value for the obtained amplitude reduction factors with the fitting tables. Also, can you please report if you stayed within the Nyquist criterium? It looks like you have more parameters (16 and maybe even 17 if So was included) used as that the data range would give you. Tables S7-S12: please give error bars and only report relevant digits.

Line 467: check again your Mn EXAFS, OH is not absorbed, but rather a Mn oxide is formed.

Response to Decision Letter

May 15, 2024

Journal: Nature Communications

Reference number: NCOMMS-23-58688A

Title: Operando Visualization of Multi-Site Synergistic H₂-Production Mechanisms on Sub-Nanometric High-Entropy Metallenes

Reviewer #1 (Remarks to the Author):

The authors have satisfactorily addressed the reviewer's comments. The revised manuscript is acceptable for publication in this journal.

Response: We thank the reviewer for the positive comments and recommendation on the publication of this work, also thanks for your previous constructive comments, which helped a lot for the improvement of this work.

Reviewer #2 (Remarks to the Author):

In the revised manuscript, the authors addressed some comments from the reviewer. The updated results in Supplementary Table 5 are very solid now. However, the authors still had some concerns in the computational part.

Response: We greatly appreciate your approval of our previous revisions. Based on your comments and suggestions, we further revised our manuscript carefully. All changes have been highlighted in the revised manuscript by formatting the text in Yellow color. Detailed lists of revisions are listed below:

Q1. In the computational method, the Monkhorst-Pack k-point mesh of $3 \times 2 \times 1$ was adopted in this work. However, the cell parameters of $a=b=10.58010 \text{ \AA}$, and $c=21.84430 \text{ \AA}$ were used. It is weird that a is equal to b but the k-point mesh along a and b are not equal. Please double check this computational setup.

Response: Thanks for your reminder. Based on the previous experiences, the configuration of the k-point mesh is determined by the cell parameters, with the condition that $a=b$ requires a k-point count exceeding 20. As an initial step, we opted for a $2 \times 2 \times 1$ k-point mesh to conduct preliminary tests. Furthermore, we undertook a K-point convergence study using varied meshes ($3 \times 2 \times 1$, $2 \times 3 \times 1$, $3 \times 3 \times 1$, $3 \times 4 \times 1$, and $3 \times 4 \times 1$), and the resultant energy variations were illustrated in Figure R1 and Table R1. This analysis unequivocally demonstrates that convergence is nearly achieved with k-point meshes of $3 \times 2 \times 1$, $2 \times 3 \times 1$, $3 \times 3 \times 1$, $3 \times 4 \times 1$, and $3 \times 4 \times 1$. To optimize both computational time

and energy consumption, we ultimately selected the 3×2×1 k-point mesh for our studies. Indeed, your recommendation is an excellent parameter setting.

Table R1. K-piont of HEA.

K-point parameter	Energy (eV)
2×2×1	844.054150558
3×2×1	831.054150615
2×3×1	831.054050622
3×3×1	831.054050634
3×4×1	831.054050632
4×4×1	831.054050641

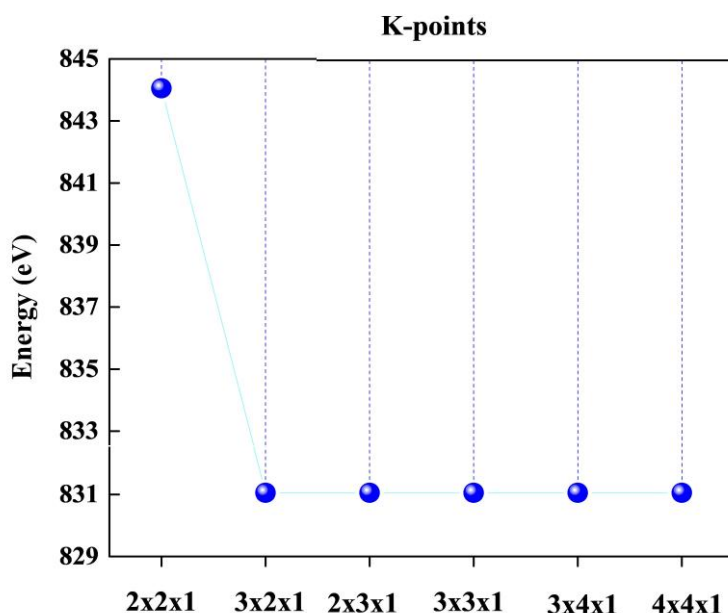


Figure R1. Correspondence curve of K-piont of HEA.

Q2. In DFT part, the authors pointed out ‘Rh top site has the lowest ΔG_{H^*} (-0.132 eV) relative to other comparison sites. However, the ΔG_{H^*} was predicted to be more negative on other sites in Figure 5c. This result turns out that Rh site is the most active site to promote HER, but it cannot prove that hydrogen prefers to be adsorbed on Rh site. Based on Figure 5c, Pd2 site exhibits the lowest value of ΔG_{H^*} , implying that hydrogen prefers to be adsorbed on this site. If the authors want to highlight the activity enhancement of HEA, it is suggested to compare the average ΔG_{H^*} even though it is not very accurate to evaluate the HER activity of HEA.

Response: Thanks for your suggestion. According to the Sabatier principle, deviations from an optimal value will lead to variations in the strength of interaction between the intermediate and

catalyst. When the ΔG_{H^*} value approaches zero, it indicates excellent performance of HER electrocatalyst. Figure 5c demonstrates that Rh1 and Rh2 exhibit lower ΔG_{H^*} values compared to Pd1 and Pd2, approaching zero. Therefore, it can be inferred that Rh is a highly probable catalytic activation center. However, solely relying on this graph does not allow us to determine whether H_2 has a greater affinity for attaching to Rh. When comparing secondary elements, it is logical to evaluate samples with superior performance. Your suggestion of employing average ΔG_{H^*} as a descriptor for evaluating HER electrocatalysts is both innovative and feasible in my opinion. In our subsequent work, we will conduct a theoretical approach to make comparisons accordingly. Thank you again for your good advice.

Q3. Please check the Figure 5c. The color of the solid line is not consistent with that of the dash line.

Response: I apologize for this error. We have changed the color in the Figure 5c. The solid lines are consistent with dash lines now. The updated Figure 5c is presented in the revised Manuscript. Thanks again for your reminder.

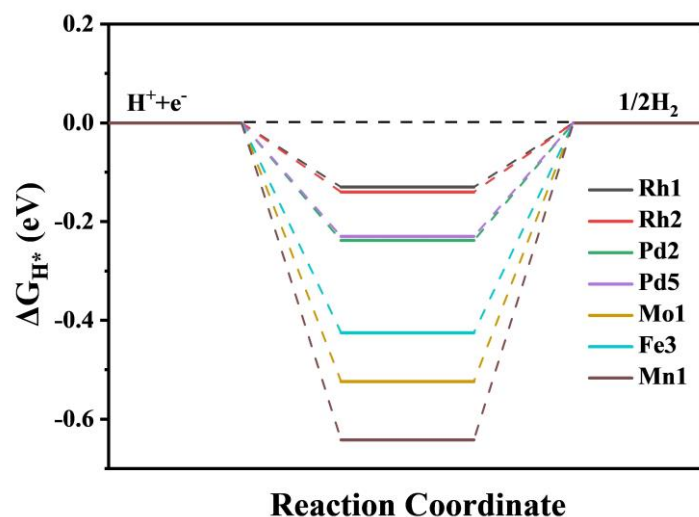
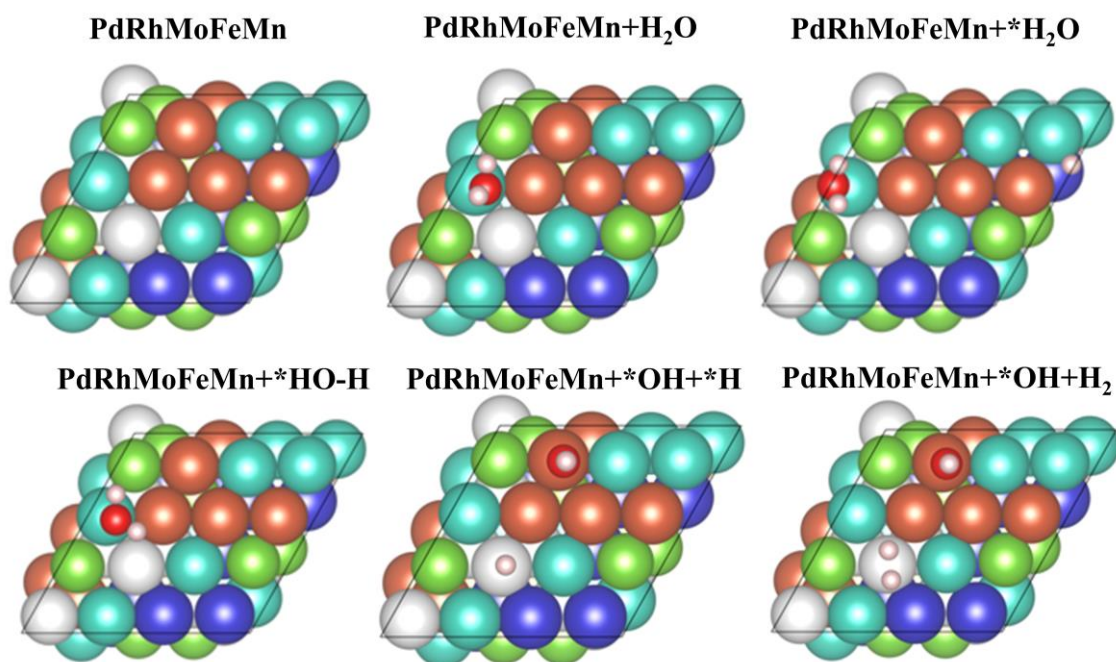


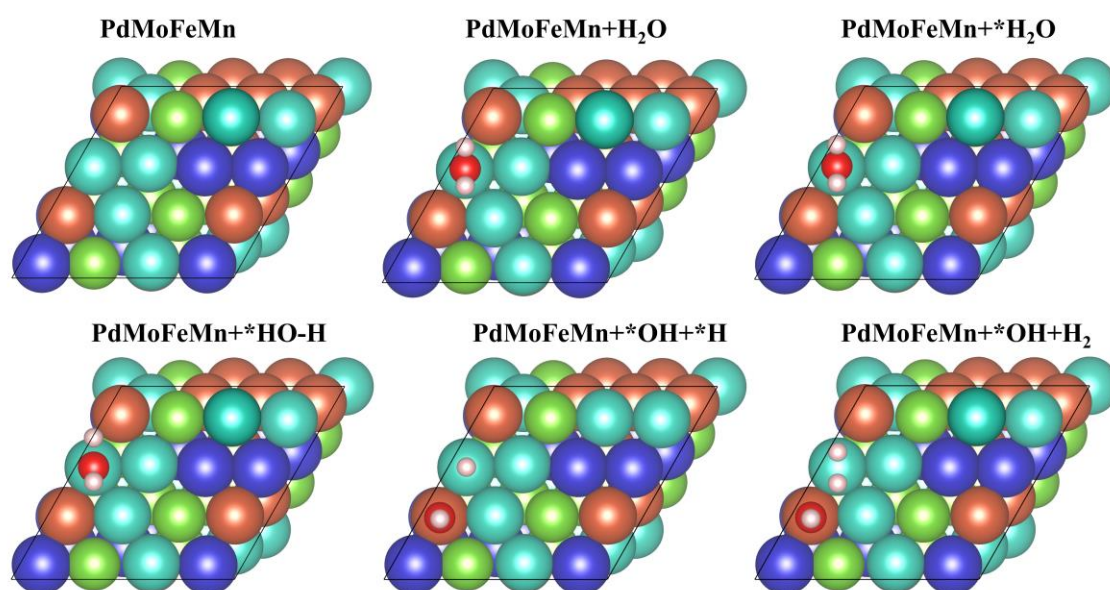
Figure 5c. The ΔG_{H^*} profiles on various catalytic sites of PdRhMoFeMn HEMs.

Q4. In Supplementary Figure 37-40, please mark the name of the structure corresponding to that in Figure 5h. Moreover, please check if H-OH is adsorbed on the surface. If so, please change it to ‘*H-OH’ in Figure 5h.

Response: Thanks for your suggestions. We have marked the corresponding name of each structure in Supplementary Figure 42-45. In addition, we have carefully checked the H-OH state. It is adsorbed on the catalyst surface. Thus, we have changed it to ‘*H-OH’ in Figure 5h.

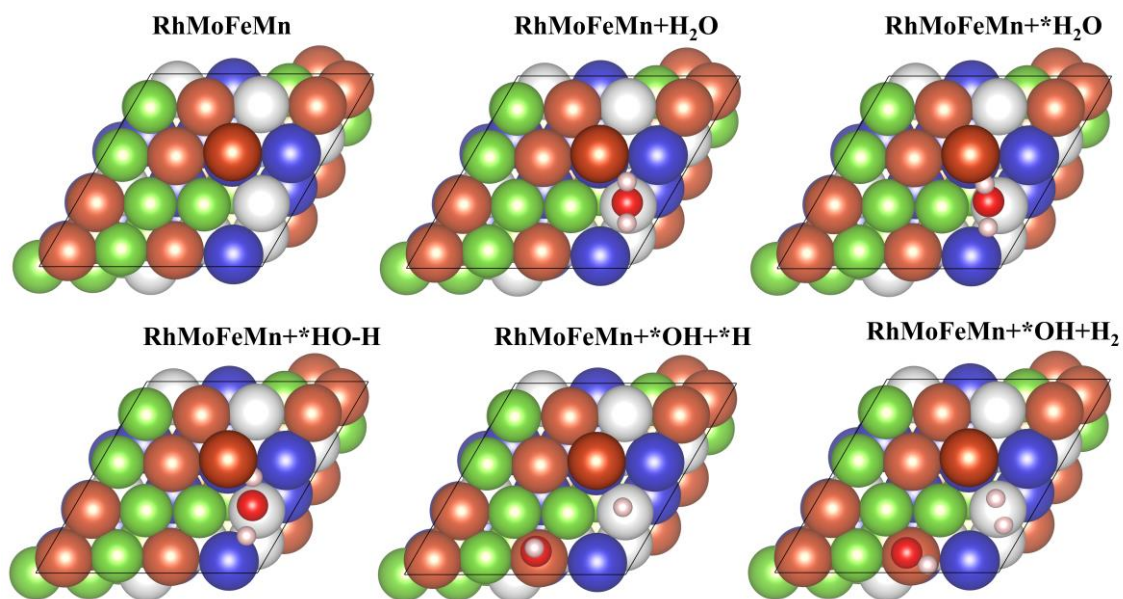


Supplementary Fig. 42 The DFT calculated structural models of water dissociation on PdRhMoFeMn HEMs.

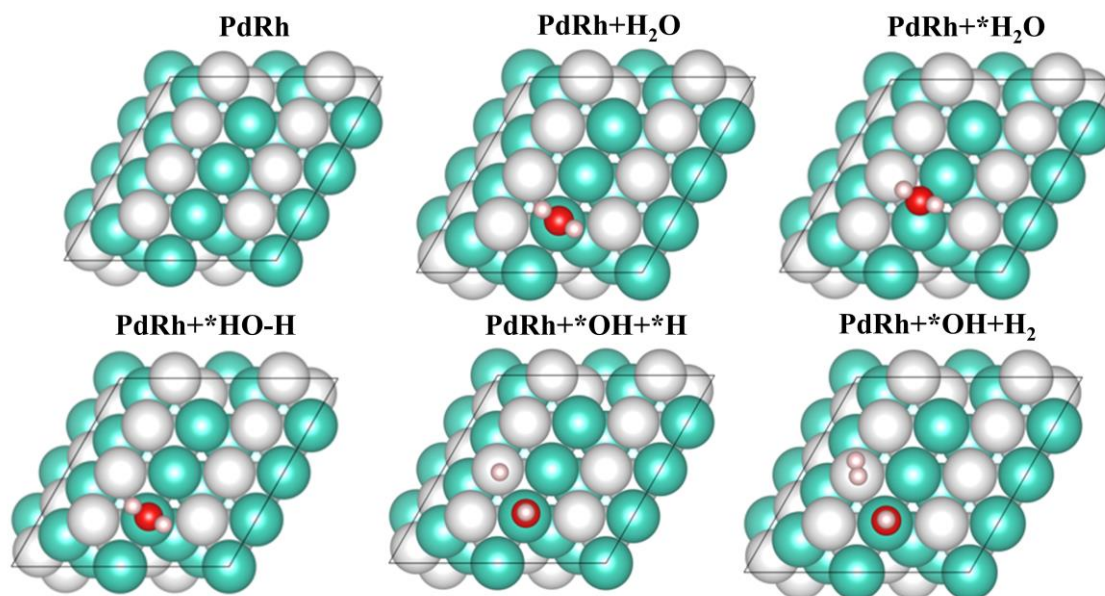


Supplementary Fig. 43 The DFT calculated structural models of water dissociation on

PdMoFeMn metallenes.



Supplementary Fig. 44 The DFT calculated structural models of water dissociation on RhMoFeMn metallenes.



Supplementary Fig. 45 The DFT calculated structural models of water dissociation on PdRh metallenes.

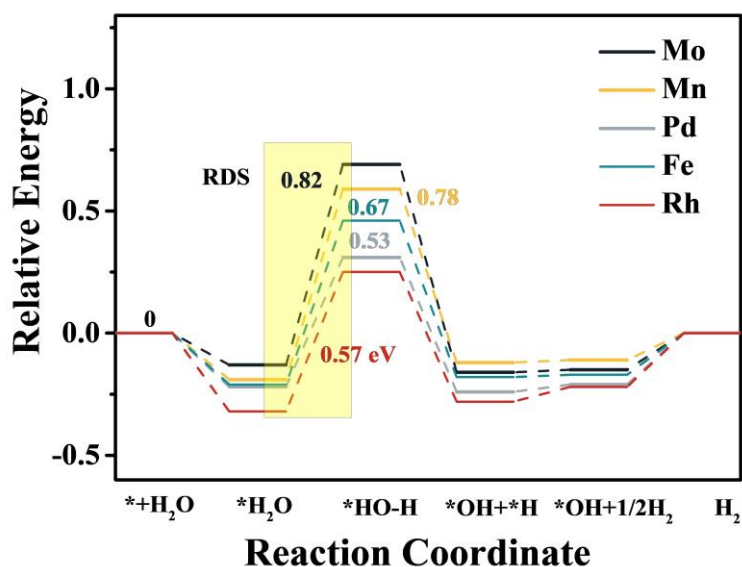


Figure 5h. The reaction energy profile for water dissociation on various catalytic sites of PdRhMoFeMn HEMs.

Q5. In Supplementary Figure 41, the energy of ‘OH +*’ is much lower than of ‘*OH’. The reviewer is surprised by this result since the energy of isolated OH (which is a radical) should be very high. Please check this result.

Response: Thanks for your valuable question. We have paid attention on the issue of OH as a free radical and investigate its potential energy. As shown in Figure R2, our test findings demonstrate that OH radical is about 0.28 eV in the standard state (298.15 K, 1 atmosphere). It is not very high as you mentioned. According to Table R2, the total energy of *+OH is lower than that of *OH. Therefore, we think our result is correct.

```

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501
+----- Tip -----+
This Feature Was Contributed by Nan XU, Qiang LI and Jincheng LIU.
See An Example in vaspkit/examples/thermo_correction/ORR.
Only vibrations! No Translation & Rotation & Electron contributions.
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Please Enter The Temperature (K):

----->>
298.15
-->> (01) Reading OUTCAR File...
+----- Summary -----+
Neglect PV contribution to translation for adsorbed molecules.
To avoid abnormal entropy contribution,
frequencies less than 50 cm-1 are set to 50 cm-1.
U(T) = H(T) = ZPE + Delat_U(0->T)
G(T) = H(T) - TS = ZPE + Delat_U(0->T) - TS

Temperature (T): 298.1 K
Zero-point energy E_ZPE      :      6.496 kcal/mol      0.281703 eV
Thermal correction to U(T):    6.571 kcal/mol      0.284956 eV
Thermal correction to H(T):    6.571 kcal/mol      0.284956 eV
Thermal correction to G(T):    6.479 kcal/mol      0.280937 eV
Entropy S                    :      1.301 J/(mol*K)      0.000013 eV/K
Entropy contribution T*S      :    387.759 J/(mol)      0.004019 eV
+-----+
0-----0
|          * ACKNOWLEDGMENTS *          |
| Other Contributors (in no particular order): Peng-Fei LIU, |
| Xue-Fei LIU, Dao-Xiong WU, Zhao-Fu ZHANG, Tian WANG, Qiang LI, |
| Ya-Chao LIU, Jiang-Shan ZHAO, Qi-Jing ZHENG, Yue QIU and You! |
| Advisors: Wen-Tong GENG, Yoshiyuki KAWAZOE |
| :) Any Suggestions for Improvement are Welcome and Appreciated (: |
|-----|
|          * CITATIONS *          |
| When using VASPKIT in your research PLEASE cite the paper: |
| [1] V. WANG, N. XU, J.-C. LIU, G. TANG, W.-T. GENG, VASPKIT: A |
| User-Friendly Interface Facilitating High-Throughput Computing |
| and Analysis Using VASP Code, Computer Physics Communications |
| 267, 108033, (2021), DOI: 10.1016/j.cpc.2021.108033 |
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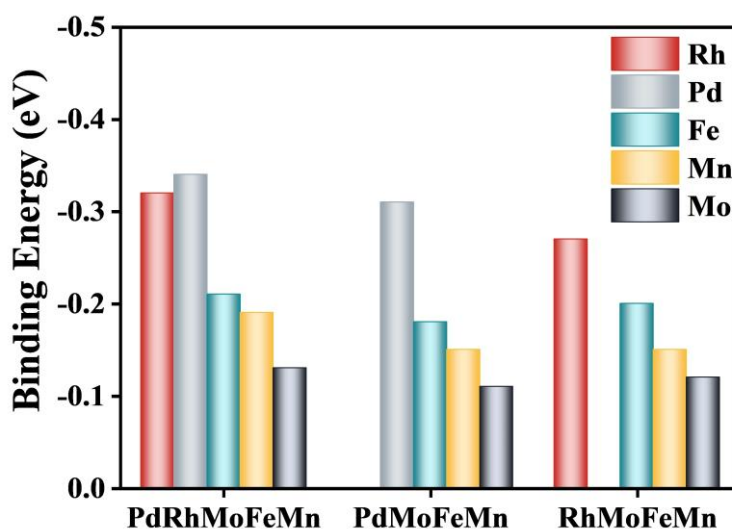
Figure R2. Screenshot of calculation result.

Table R2. The detail energy profile of the PdRhMoFeMn, PdMoFeMn, RhMoFeMn and adsorbed intermediates.

Name	Delta G	*OH	*	OH
PdRhMoFeMn	-0.81024	832.14533	831.05415	0.28094
PdMoFeMn	-0.85123	832.18632	831.05415	0.28094
RhMoFeMn	-1.13989	832.47498	831.05415	0.28094

Q6. In Supplementary Figure 42, the reviewer highlighted that the results were from NEB. The reviewer is confused about how to use NEB calculations to predict binding energy. Please provide more details about it.

Response: Thank you for reminding us. Nudged Elastic Band (NEB) is a method used to find transition states (TS) in chemical reactions. We made a mistake and noted it incorrectly. We have corrected it in the revised Manuscript. I apologize for any inconvenience caused.



Supplementary Fig. 47 The binding energy profile for water adsorption on PdMoFeMn, RhMoFeMn, and PdRhMoFeMn.

Finally, we hope that all concerns have been addressed. Thank you very much again for your attention and kindness to improve our work.

Reviewer #3 (Remarks to the Author):

I have thoroughly read the revised manuscript and the reply to reviewers. In general, most of my questions have been addressed. However, while I thank the authors for now including the fits of the EXAFS spectra (this was really missing), the discussion of the fitting results and XAS data in general needs some further thoughts as the only real novelty of this manuscript is that some structure-performance relationships might be deciphered from the data.

Response: We thank you for your insightful comments, which are of great significance to the improvement of our work. Based on these additional comments, we have done corresponding revisions carefully by supplementing more new data. All changes have been highlighted in the revised manuscript by formatting the text in Yellow color. Detailed lists of revisions are listed below:
Additional (minor) comments:

Q1. Page 4, line 77: ‘challenging’ in what respect?

Response: Thanks for your comment. Different metallic elements differ in size, crystal structure, and electronegativity, resulting in varying degrees of lattice mismatch between them, which is not conducive to the formation of high-entropy alloy materials without phase separation. In addition, high-entropy two-dimensional materials are rarely reported. Due to these factors, using different metal atoms to construct ultrathin high-entropy two-dimensional materials is a challenging task.

Q2. Page 4, line 89, there is quite a bit of literature on the application of XAS to study the dynamics of bimetallic systems. Please rephrase.

Response: Thanks for your valuable suggestion. We have included the bimetallic system, added the corresponding references [Science 366, 850-856 (2019); Nat. Commun. 13, 2486 (2022)] and re-edited this sentence in the revised Manuscript.

Line 88: Nevertheless, most of these techniques are applied to the analysis of single-atom and bimetallic catalytic reaction systems due to their clear and well-defined coordination structures³⁴⁻³⁸.

Q3. Fig 2d and line 216: The absence of other phases in XRD does not mean no additional phases are formed, XRD only detects crystalline phases larger as 3 nm, no amorphous phases.

Response: Thanks for your valuable comments. We agree with you. Amorphous phases and the crystal phases of too small particles are difficult to detect due to the sensitivity limitation of XRD instruments. Therefore, the absence of other phases in XRD does not fully prove the successful preparation of HEAs. However, we also performed HRTEM, ACTEM and aberration corrected EDS elemental mapping tests. These results indicate that there are no obvious cluster aggregations

on PdRhMoFeMn HEMs and the Pd, Rh, Mo, Fe, and Mn elements are uniformly dispersed throughout the HEMs. XRD combined with these characterization techniques mentioned above jointly proves the successful construction of PdRhMoFeMn HEMs, which is the same as the usual method reported in the literature to confirm the formation of HEA [Nat. Commun. 14, 4182 (2023); Nat Commun 12, 6261 (2021); J. Am. Chem. Soc. 144, 10582-10590 (2022)].

Q4. Page 8, line 166: Well, the peaks are not yet corrected for phase shifts. You should refer here to your fitting results, which do indicate Rh-Rh and Pd-Pd neighbours, suggesting the presence of small clusters. Actually, the Rh-Rh distance is really close to that in foil and the Pd-Pd distance is not too far off, likely as a result of the observed distortions of the structure due to the smaller atoms present.

Response: Thank you for the reviewer's suggestion. We have adjusted the relevant values and labeled them with phase correction in Figures 3b and 3d. Figures 3b and 3d show the prominent peaks at ~ 2.75 Å for Pd-M and Rh-M, where M can be Pd, Rh, Mo, Fe, or Mn. Due to the thinness of the material, lower coordination numbers and a homogeneous distribution of metal atoms, it is indeed possible to observe Rh-Rh and Pd-Pd neighbors, which is consistent with the literature reported [Nat. Commun. 13, 2662 (2022); J. Am. Chem. Soc. 143, 17117-17127 (2021)]. This does not violate the definition of a high entropy alloy either. Additionally, the relatively large atomic numbers of Pd and Rh result in smaller variations caused by other smaller atoms (Mo, Fe and Mn).

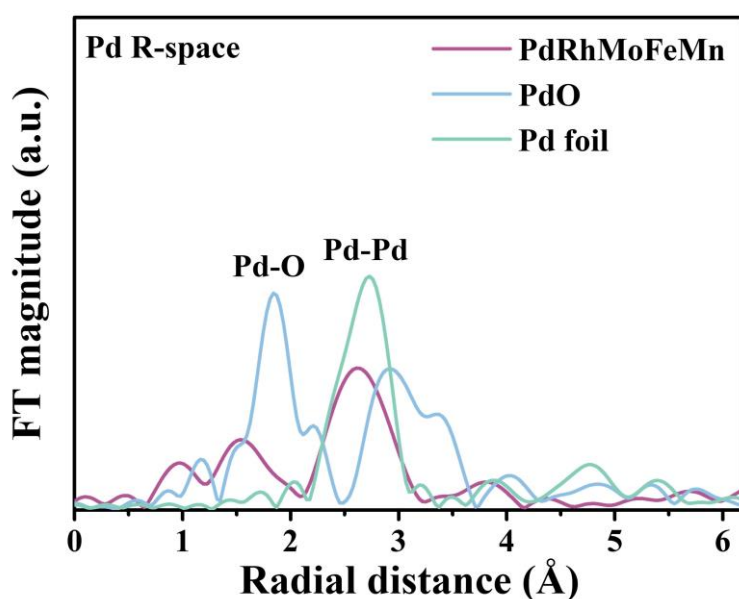


Figure 3b. The Pd FT EXAFS spectra of PdRhMoFeMn HEMs, PdO, and Pd foil with phase correction.

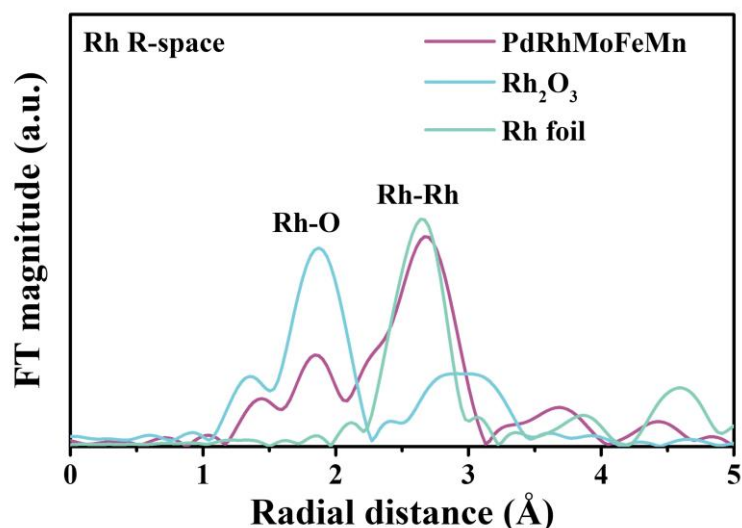


Figure 3d. The Rh FT EXAFS spectra of PdRhMoFeMn HEMs, Rh₂O₃, and Rh foil with phase correction.

Q5. The Pd-O and Rh-O contributions observed are direct bonds at well-defined bond distances. If this was O from the electrolyte you would not observe such a well-defined bond. So, most likely these are Pd-O and Rh-O bonds directly at the surface of the HEMs as you have no further indication of oxidation of Pd and Rh (L edges are much more sensitive). However, XPS indicates surface oxide as well. Please incorporate this observation in your manuscript as the surface chemistry influences the reaction mechanism.

Response: Some literature has reported that in strong alkaline solutions, a slight amount of oxygen from the electrolyte can be observed at OCP state [ACS Energy Lett. 4, 2813-2820 (2019)]. Due to the ultra-thin thickness of HEMs, we consider it reasonable to observe some oxygen contributed by the electrolyte at OCP condition. In the research system of this article, the object of our research is the metallic high-entropy alloys as the host material, which is the active site of this material and the source of its excellent HER activity. For HER, the less active trace surface oxygen is negligible, and many reports do not take surface oxygen into account [Nat. Commun. 13, 2662 (2022); Nat. Commun. 15, 359 (2024); Adv. Mater. 36, 2309715 (2023)]. According to previous reports, the HER activity of metal oxides is usually very poor. Its contribution to the activity of the overall material is very small. We also tested the HER performance of PdO and RhO₂. As shown in Figure R3a, the HER activity of PdRhMoFeMn HEMs is far superior to PdO and RhO₂. In detail, PdRhMoFeMn HEMs only require an overpotential of 6 mV at 10 mA cm⁻², much lower than those of PdO (211 mV) and RhO₂ (169 mV) (Figure R3b). Our additional DFT calculations in Figure R5

also show that the ΔG_{H^*} of PdRhMoFeMn HEMs has almost no change after the introduction of MnO. Therefore, for HER, we believe that it is reasonable to ignore the participation of trace amounts of surface oxygen, which will have little impact on the research content and conclusions of this article.

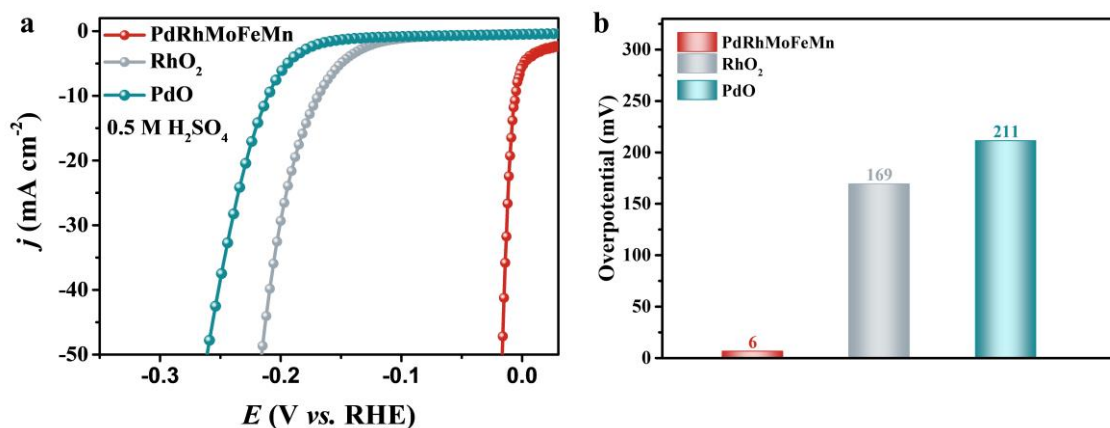


Figure R3. (a) Polarization curves and (b) the histogram for overpotentials at 10 mA cm⁻² of PdRhMoFeMn HEMs, RhO₂, and PdO in 0.5 M H₂SO₄ electrolyte.

Q6. Line 187: why contrastively? Your (XPS and EXAFS fits) data clearly suggest that Pd and Rh are also oxidized at the surface.

Response: Thanks for your kind reminder. We agree with you that the use of the word ‘contrastively’ is inappropriate here. We have replaced ‘contrastively’ with ‘Furthermore’ in the revised Manuscript. In addition, due to the exposure of ultra-thin HEMs to air, the adsorption of trace amounts of surface oxygen on the catalyst surface is a common phenomenon, which is consistent with the reported literature [Nat. Commun. 13, 2662 (2022); Nat. Commun. 11, 5437 (2020)].

Q7. Synthesis procedure: at what concentrations were the different elements initially mixed? Does that correspond to the measured ratio by ICP-OES?

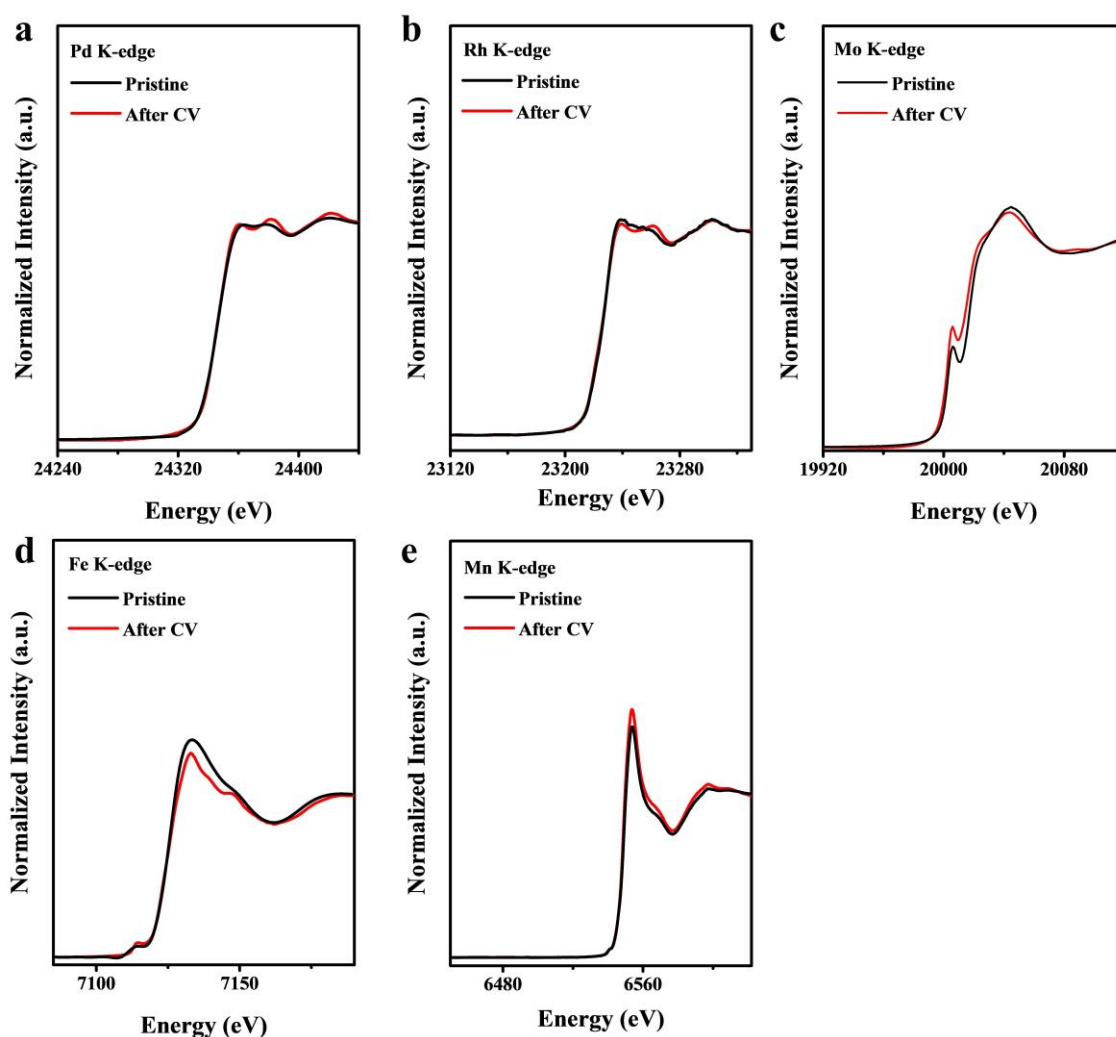
Response: Thanks for your comment here. In the initial mixed solution, the contents of Pd, Rh, Mo, Fe, and Mn precursors are 0.0312, 0.0310, 0.0328, 0.0256, and 0.1326 mmol, respectively. Due to the different ease of reduction of different metal precursors, the initial feed ratio and the ratio of the final product are different, which is also similar to the reported literature results [Nat. Sci. Rev. 8, nwab019(2021); Adv. Mater. 34, 2105276 (2022)].

Q8. Line 263: aggregation of carbon or of the HEM? Do you have the XAS spectra after 10000 cycles, this is the best probe to show local structure change? Your Mn EXAFS data (fits are missing)

clearly suggest the formation of a Mn oxide, which then suggest significant structural changes within the HEM on the local scale.

Response: Thanks for the reviewer's valuable suggestions. Supplementary Fig. 18a, b show that the dispersion of PdRhMoFeMn HEMs on carbon black did not change significantly before and after the stability test, and there was no obvious aggregation of HEMs on carbon black. The aggregation observed by the reviewer may be the aggregation of carbon caused by differences in sample dispersion on the TEM copper grid.

Based on the reviewer's suggestion, we have added the XAS spectra after 10000 cycles. As shown in Supplementary Fig. 19, there are no significant changes observed in the XANES spectra of each element after 10000 cycles. Additionally, we have fitted all operando Mn EXAFS spectra in various electrolytes and observed that the most significant changes in Mn-O coordination occur under alkaline conditions, likely due to the gradual adsorption of OH under OCP conditions. As the potential increases, OH gradually increases, leading to the formation of Mn-related oxides. Similar results are also observed in PBS. O from the electrolyte was observed in Pd, Rh, and Mn, but only Mn formed obvious oxides in the end.



Supplementary Fig. 19 The XAS Characterization of PdRhMoFeMn HEMs before and after 10,000 CV cycles. The XANES spectra of (a) Pd, (b) Rh, (c) Mo, (d) Fe, and (e) Mn before and after 10,000 CV cycles.

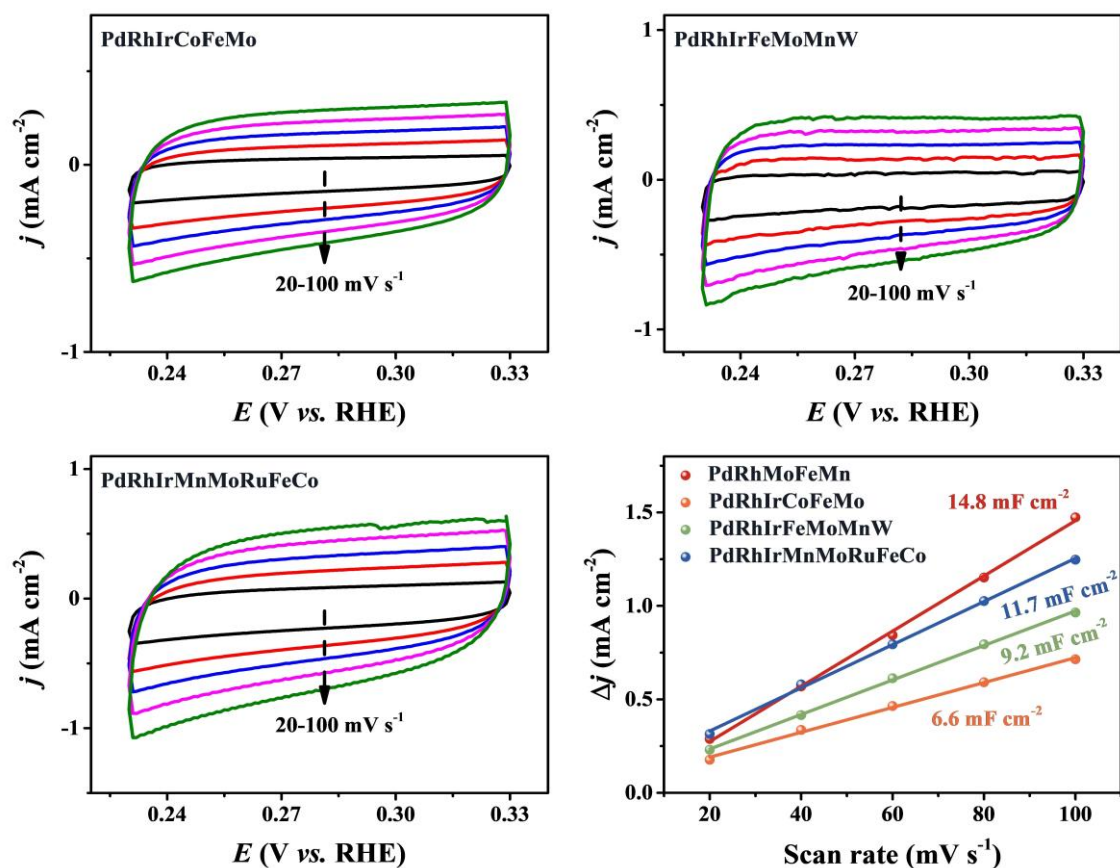
Line 266: Supplementary Fig. 19 also shows that there are no significant changes observed in the XANES spectra of each element after 10,000 cycles, further suggesting the robustness of their electronic structure and valence state.

Q9. Line 327: ‘presumably due to better atom utilization’, there is no direct proof for this.

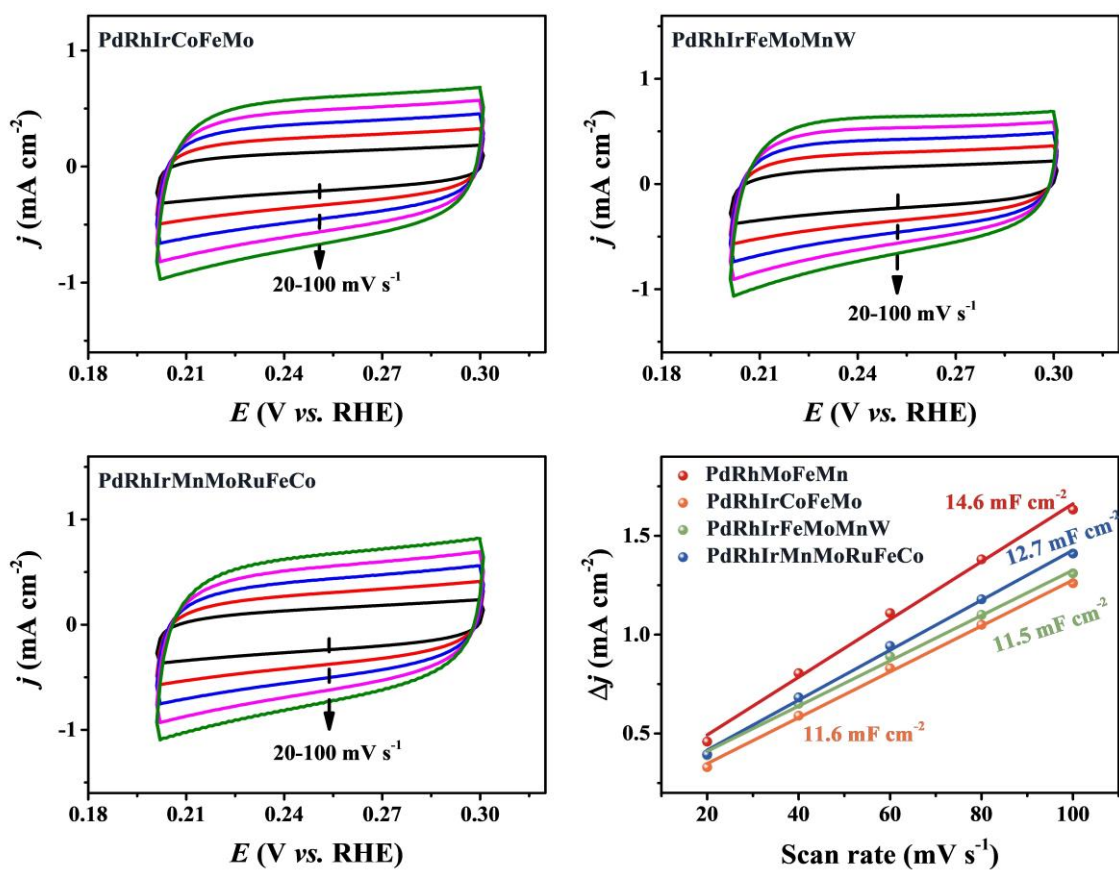
Response: Thanks for your professional suggestions. Based on your comments, we have supplemented the electrochemical double-layer capacitance (C_{dl}) tests of senary PdRhIrCoFeMo, septenary PdRhIrFeMoMnW, and octonary PdRhIrMnMoRuFeCo HEMs. Supplementary Figs. 29-31 show that PdRhMoFeMn HEMs exhibit the C_{dl} values of 14.8, 14.6 and 19.0 mF cm^{-2} , superior to senary PdRhIrCoFeMo (12.6, 3.9 and 15.8 mF cm^{-2}), septenary PdRhIrFeMoMnW (4.4, 7.1 and 8.1 mF cm^{-2}), and octonary PdRhIrMnMoRuFeCo (2.8, 6.4 and 6.2 mF cm^{-2}) in 0.5 M H_2SO_4 , 1.0

M PBS, and 1.0 M KOH electrolytes, respectively, suggesting the higher atomic utilization efficiency of PdRhMoFeMn HEMs.

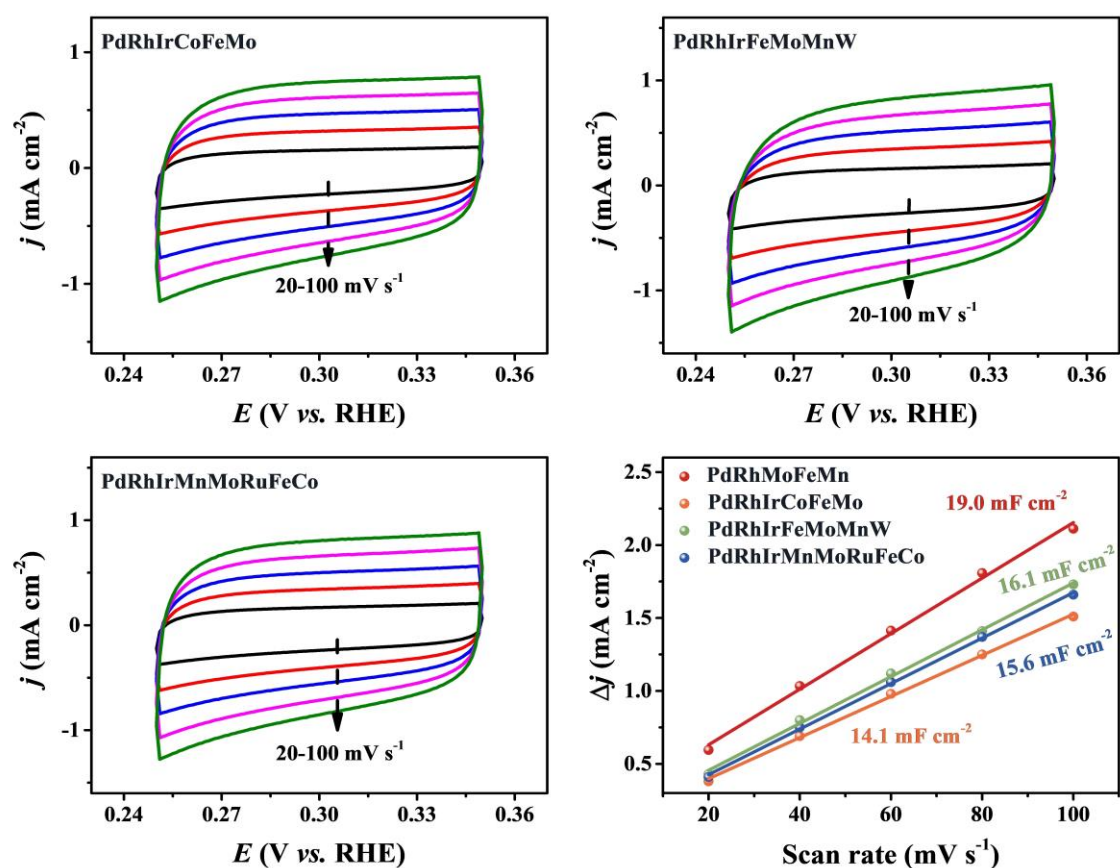
Line 327: PdRhMoFeMn HEMs have the larger C_{dl} values than senary, septenary, and octonary HEMs over a wide pH range, proving the higher atomic utilization efficiency of PdRhMoFeMn HEMs (Supplementary Figs. 29-31).



Supplementary Fig. 29 CV plots and C_{dl} in 0.5 M H_2SO_4 electrolyte. CV plots of (a) senary PdRhIrCoFeMo, (b) septenary PdRhIrFeMoMnW, and (c) octonary PdRhIrMnMoRuFeCo HEMs at varying scan rates from 20 to 100 mV s⁻¹ in 0.5 M H_2SO_4 electrolyte. (d) C_{dl} of these nanocatalysts in 0.5 M H_2SO_4 electrolyte.



Supplementary Fig. 30 CV plots and C_{dl} in 1.0 M PBS electrolyte. CV plots of (a) senary PdRhIrCoFeMo, (b) septenary PdRhIrFeMoMnW, and (c) octonary PdRhIrMnMoRuFeCo HEMs at varying scan rates from 20 to 100 mV s⁻¹ in 1.0 M PBS electrolyte. (d) C_{dl} of these nanocatalysts in 1.0 M PBS electrolyte.



Supplementary Fig. 31 CV plots and C_{dl} in 1.0 M KOH electrolyte. CV plots of (a) senary PdRhIrCoFeMo, (b) septenary PdRhIrFeMoMnW, and (c) octonary PdRhIrMnMoRuFeCo HEMs at varying scan rates from 20 to 100 mV s⁻¹ in 1.0 M KOH electrolyte. (d) C_{dl} of these nanocatalysts in 1.0 M KOH electrolyte.

Q10. Line 354: check grammar of this new sentence.

Response: Thanks for your careful checks. We are sorry for our carelessness. We have corrected it in the revised Manuscript.

Changes to the main text:

Line 356: As displayed in Supplementary Fig. 39 and Supplementary Table 6, the ΔG_{H^*} of PdRhMoFeMn is -0.132 eV, which is significantly higher than that of PdRh (-0.528 eV) and RhMoFeMn (-0.465 eV).

Q11. Line 354: How does deltaG for Rh change if the coordination around Rh changes from a homogeneous HEM to one with clusters (and Mn/Fe oxide).

Response: Thank the reviewer for the valuable suggestion. Based on your suggestion, we have added the calculation of the Gibbs free energy of hydrogen adsorption (ΔG_{H^*}) for a homogeneous HEM with MnO clusters (MnO/ PdRhMoFeMn HEMs). Figure R4 shows the top and side view computational modeling of MnO/ PdRhMoFeMn HEMs. As displayed in Figure R5, the ΔG_{H^*} of

MnO/ PdRhMoFeMn HEMs is -0.13 eV, which is close to that of PdRhMoFeMn HEMs (-0.132 eV). This result shows that the formation of trace oxide clusters during the reaction has minimal impact on its ΔG_{H^*} .

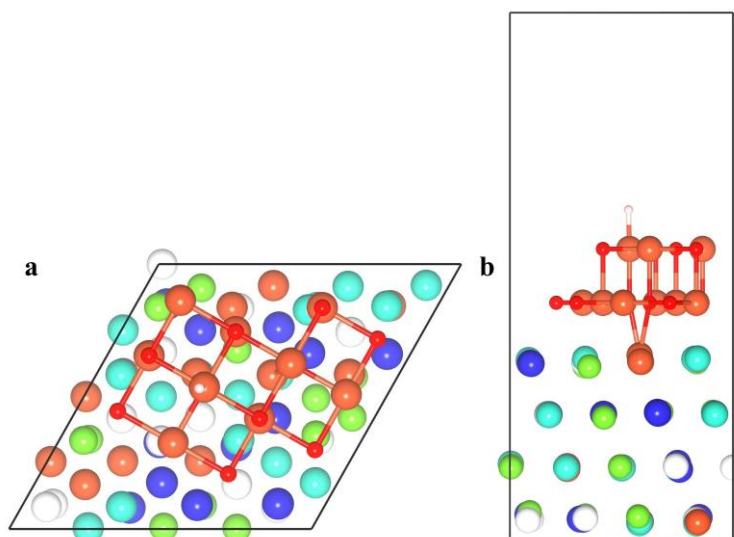


Figure R4. (a) Top and (b) side view computational modeling of MnO/ PdRhMoFeMn HEMs.

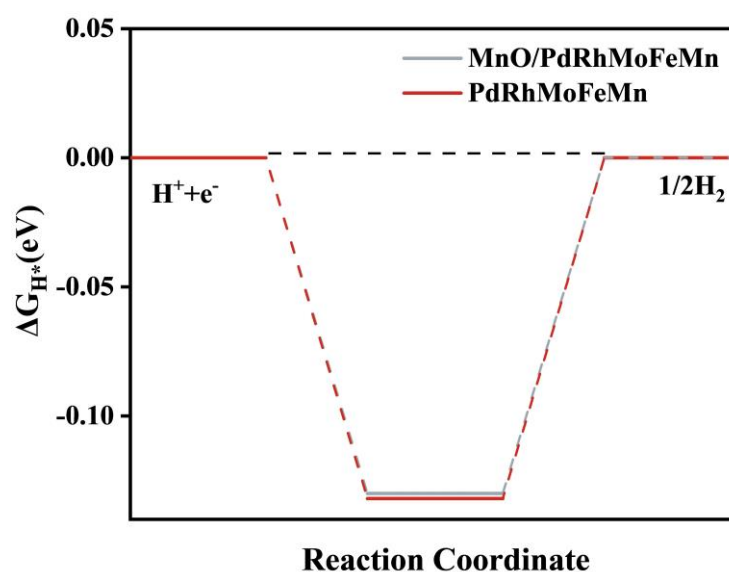


Figure R5. The ΔG_{H^*} profiles of PdRhMoFeMn and MnO/ PdRhMoFeMn HEMs.

Q12. Line 405: really not clear what you mean by ‘scattered data’ (which is only presented in Figure S46, not S44-46 as stated in the text).

Response: Thank you for your careful reading. Only Figure 46 shows the scattered data. We have changed it accordingly.

Line 407: Supplementary Figs. 49-51 demonstrate the consistency of data processing and well-normalization across a wide range of XANES spectra.

Q13. Line 412: what do you mean by ‘enhanceive electronic intensity’? Do you means enhanced

electron density?

Response: Thanks for your question. What we want to express is that the decrease in the white line intensity of Pd and Rh indicates that their electron density increases after applying reduction potential. We have corrected it to ‘enhanced electron density’ in the revised Manuscript. We apologize for any confusion caused by the inaccurate wording here.

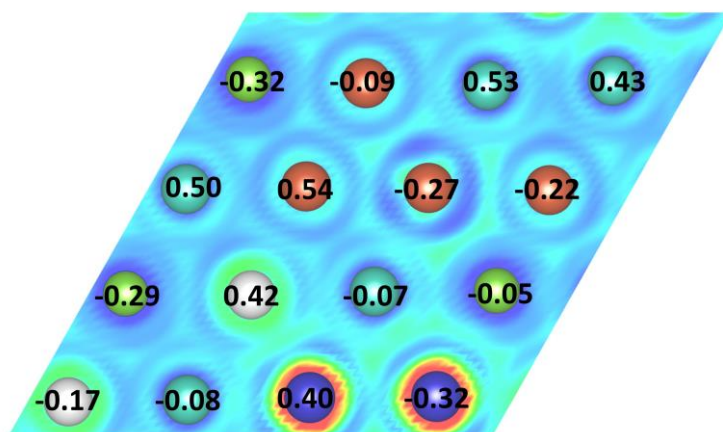
Line 413: The XANES spectra in Fig. 6c,d demonstrate a reduction in the white line intensity of both Pd and Rh, indicating an enhanced electron density upon the application of a reduction potential.

Q14. Line 416: how about charge transfer from Fe and Mo?

Response: Thanks for your valuable comments. Since the electronegativities of Fe (1.83), Mo (2.16), and Mn (1.55) are lower than those of Pd (2.2) and Rh (2.28), it is easier for Pd and Rh to obtain electrons from Fe, Mo, and Mn. In addition, we also performed Bader charge calculations to analyze the transfer of electrons between various elements in HEMs. Supplementary Fig. 36 shows that electrons are transferred from Fe, Mo, Mn to Pd and Rh in HEMs, which is consistent with reported literature [Nat Commun 13, 5497 (2022); Nat Commun 13, 2662 (2022); J. Am. Chem. Soc. 143, 17117-17127 (2021); Angew. Chem. Int. Ed. 2022, 134, e202205923].

Changes to the main text:

Line 345: Supplementary Fig. 36 shows that electrons are transferred from Fe, Mo, Mn to Pd and Rh in HEMs due to the lower electronegativity of Fe, Mo, Mn.



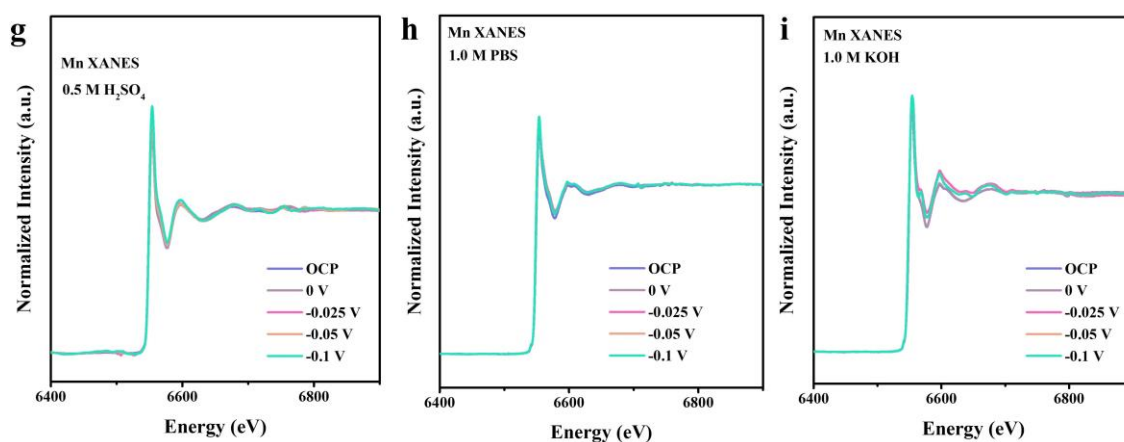
Supplementary Fig. 36 The Bader charge analysis of PdRhMoFeMn HEMs.

Q15. Line 417 and Figure S47 and related discussion on formation of hydroxyl groups at Mn: Not sure how to interpret this, definitively not a consistent behaviour over the pH range. A) the changes here might just be a normalization problem. The edge energy seems to be the same. B) here the

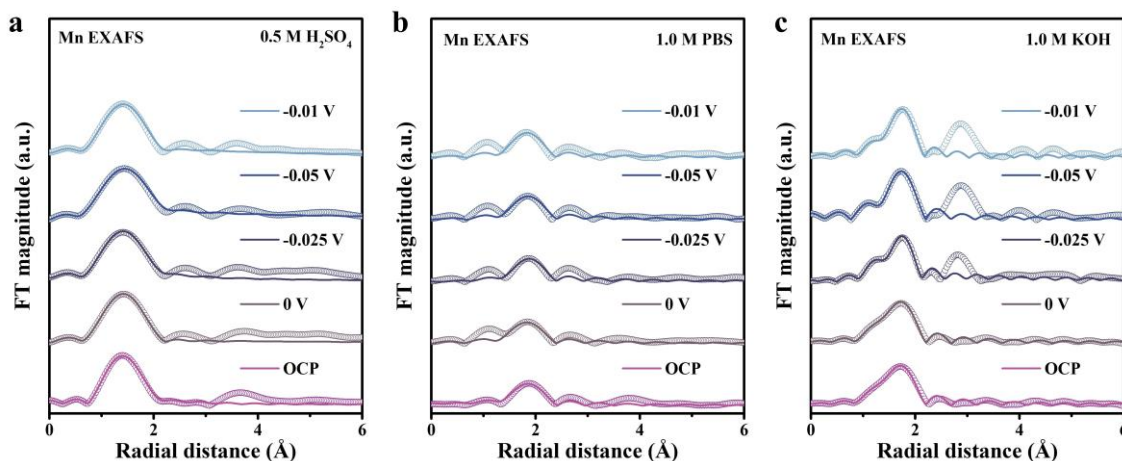
overall coordination of Mn changes as well: what happens here? EXAFS suggest formation of Mn oxide, suggesting significant reordering of the HEM as a result C) this is a very small change in oxidation state, but at the same time large changes in the EXAFS suggesting the same structural reordering as in B. Forming of a significant Mn oxide is not the same as formation of OH groups on Mn. Please discuss.

Response: Thanks for your valuable comments.

(A) Thanks for your suggestion. We have rechecked the normalization and found no issues with it. Therefore, some variations are likely due to reactions with the electrolyte. Similarly, such behavior is also observable in the EXAFS data.



Supplementary Fig. 49 The broad range XANES spectra of (g-i) Mn in different electrolyte.



Supplementary Fig. 56 Operando Mn EXAFS spectra of (a) 0.5 M H₂SO₄, (b) 1.0 M PBS and (c) 1.0 M KOH without phase correction. The detailed fitting results are listed in Supplementary Tables 13-15.

(B) We observed a significant amount of OH adsorption at the OCP. As the potential is applied, we can observe more OH adsorption, leading to the formation of additional Mn-O coordination, especially noticeable under KOH conditions.

(C) In both alkaline and neutral conditions, the changes in XANES spectra are clearly observable and well normalized (Supplementary Fig. 49g-i). This consists with the EXAFS results (Supplementary Fig. 56), indicating OH adsorption at the OCP state under KOH and PBS. As catalytic progresses, an increasing amount of OH adsorption leads to the observation of manganese oxides. O from the electrolyte was observed in Pd Rh Mn, but only Mn formed obvious oxides in the end.

Line 438: O from the electrolyte was observed in Pd, Rh, and Mn, but only Mn formed obvious oxides in the end.

Q16. Page 436: this is not an ‘elevation’, but an increase in peak intensity. There is more that could go in an increase in intensity as just an increase in coordination number, it could also be a decrease of the pseudo-Debye Waller factor. Here you should really go with your EXAFS fitting results. Please add this to the manuscript and discuss. Here I see a consistent fitting of Pd-O coordination numbers across the pH range.

Response: Thank you for the reviewer's comments. We have revised the sentence to indicate an increase in intensity and have distinguished the increase in coordination numbers based on the fitting results. It is indeed observed that the Pd-O coordination numbers increase in alkaline and neutral conditions, while they remain almost unchanged under acidic conditions. Therefore, the fitting of Pd-O coordination numbers is not consistent across the entire pH range, and we have included this observation in the manuscript.

Line 442: In Fig. 7c, a slight increase of the Pd-O peak intensity at 2 Å and Pd-O coordination numbers are seen under alkaline conditions, indicating the water adsorption on Pd sites and subsequent breaking of H₂O into intermediate H* and OH.

Q17. Line 443: if you get an increase in Pd-M coordination number (please check your EXAFS fits) than that suggests significant reordering of your HEM at different pH, and thus less stability of the HEM as suggested in the manuscript.

Response: Thanks for your valuable comments. As you can see in the Pd Table, the overall Pd-M coordination number in potential ranges from 6.11 to 7.18 from OCP to the highest potential. This observation is further supported by XRD and XAS spectra after CV, where there are no significant

changes observed in each element relative to OCP. Therefore, operando experiments are ideal for observing structural adaptations that allow materials to adjust to the optimal active sites. There are numerous studies in the literature that utilize in situ techniques to capture the beneficial effects of structural changes on activity. We believe structural reordering does not necessarily suggest decreased stability. In contrast, the rearrangement of catalysts dynamically is essential for achieving exceptional performance [Nat. Commun. 13, 1143 (2022)]. In addition, the electrochemical durability test of PdRhMoFeMn HEMs including the 10,000 cyclic voltammetry cycle test and the chronopotentiometry test also demonstrated its excellent stability in different electrolytes.

Q18. Line 457: k -space, not with a capital. These spectra should be k^2 weighted at most.

Response: We thank the reviewer's comments. The k^2 -weighted is a common weighted scheme, particularly useful for analyzing metal-ligand interactions in metal complexes. This is because k^2 -weighted preserves low-frequency information, while enhancing high-frequency information and does not introduce unnecessary noise. However, in high-frequency metal coordination systems, there may be very strong high-frequency vibrations. These vibrations may be more clearly displayed under k^3 -weighted. Therefore, for highlighting high-frequency features and conducting in-depth analysis of metal coordination systems, using k^3 -weighted can be very useful. Since we have a sufficient number of sampling points (energy step is 1.5 eV each point) and the oscillations in the spectrum are clear, we believe that the interference of unnecessary noise is minimal. Therefore, we consider using k^3 -weighted to analyze metal-metal bonds to be appropriate.

Q19. Supplementary 413- : please give a reference to all software packages used. For example, IFEFFIT has been called the Demeter software suite for ages now. Not quite sure I understand the fitting strategy, one cannot fit the coordination number and amplitude reduction factor simultaneously. Please report the value for the obtained amplitude reduction factors with the fitting tables. Also, can you please report if you stayed within the Nyquist criterium? It looks like you have more parameters (16 and maybe even 17 if So was included) used as that the data range would give you. Tables S7-S12: please give error bars and only report relevant digits.

Response: Thank you for the reviewer's suggestions. We utilized the Demeter software package and have included the relevant references accordingly [Ravel B., Newville M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 2005, 12 (4), 537-541]. Regarding the EXAFS measurements and analysis (see SI line 425), we apologize for any initial confusion in our statement. In the experiment, the amplitude reduction

factor for each group was fixed at 1. Therefore, we did not simultaneously fit the coordination number and amplitude reduction factor.

Regarding the Nyquist criterion, initially, our range of k and R was $3-11 \text{ \AA}^{-1}$ and $1.5-3.5 \text{ \AA}$, which indeed did not yield satisfactory results. Subsequently, we adjusted the range to $1-4 \text{ \AA}$, where $N_{\text{idp}} = (2 \times \Delta K \times \Delta R) / \pi = (2 \times 9 \times 3) / \pi = 17.19$, providing a significantly adequate value and enhancing the precision of the fitting results. We also include fitting results and error bars in the article (Supplementary Tables 7-15).

Q20. Line 467: check again your Mn EXAFS, OH is not absorbed, but rather a Mn oxide is formed.

Response: Through Mn EXAFS fitting, we observed that OH adsorption initiates at the OCP state under alkaline conditions and progressively increases with higher potentials. Similar trends were observed under PBS conditions. However, in acidic conditions, the Mn-O bond almost remains unchanged. O from the electrolyte was observed in Pd Rh Mn, but only Mn formed obvious oxides in the end.

Finally, we hope that all concerns have been addressed. Thank you very much again for your attention and kindness to improve our work.

Supplementary Table 7. Model-fitted operando EXAFS spectra results for Pd in 1.0 M KOH.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Pd-O	0.17±0.02	2.12±0.01	0.00401±0.00	-5.00±2.54	0.00464
	Pd-Pd/Rh	1.43±0.23	2.66±0.03	0.00701±0.00	1.75±8.54	
	Pd-Mo	3.68±0.18	2.81±0.04	0.00701±0.02	0.60±4.39	
	Pd-Fe/Mn	1.00±0.01	2.93±0.01	0.00701±0.01	8.31±1.66	
0 V	Pd-O	0.41±0.04	2.12±0.02	0.00401±0.01	-5.00±6.03	0.00321
	Pd-Pd/Rh	1.43±0.15	2.56±0.08	0.00701±0.02	0.71±0.33	
	Pd-Mo	3.68±0.17	2.78±0.02	0.00701±0.00	0.24±3.52	
	Pd-Fe/Mn	1.10±0.02	2.96±0.02	0.00701±0.00	8.31±1.12	
-0.025 V	Pd-O	0.53±0.09	2.12±0.03	0.00401±0.00	-5.00±6.32	0.00745
	Pd-Pd/Rh	1.43±0.12	2.56±0.01	0.00701±0.02	0.51±3.76	
	Pd-Mo	3.68±0.45	2.78±0.04	0.00701±0.01	0.06±6.07	
	Pd-Fe/Mn	1.32±0.01	2.96±0.02	0.00701±0.01	8.31±0.83	
-0.05 V	Pd-O	0.64±0.11	2.12±0.02	0.00401±0.00	-5.00±2.23	0.00549
	Pd-Pd/Rh	1.43±0.31	2.66±0.03	0.00701±0.01	3.02±0.04	
	Pd-Mo	3.68±0.37	2.82±0.02	0.00701±0.01	0.24±5.77	
	Pd-Fe/Mn	1.39±0.02	2.91±0.01	0.00701±0.01	8.31±2.52	
-0.1 V	Pd-O	0.66±0.08	2.12±0.01	0.00401±0.01	-5.00±4.12	0.00419
	Pd-Pd/Rh	1.43±0.01	2.68±0.05	0.00701±0.01	3.38±9.36	
	Pd-Mo	3.68±0.45	2.82±0.04	0.00701±0.00	0.98±6.94	
	Pd-Fe/Mn	1.41±0.01	2.93±0.01	0.00701±0.01	8.31±7.23	

Supplementary Table 8. Model-fitted operando EXAFS spectra results for Pd in 1.0 M PBS.

Sample	Path	CN	R (Å)	$\sigma^2(\text{Å}^2)$	E0	R-factor
OCP	Pd-O	0.16±0.02	2.12±0.02	0.00401±0.00	-5.00±1.00	0.00318
	Pd-Pd/Rh	1.43±0.10	2.67±0.03	0.00701±0.03	7.16±3.72	
	Pd-Mo	3.68±0.59	2.82±0.03	0.00701±0.00	4.01±0.59	
	Pd-Fe/Mn	1.00±0.15	2.89±0.03	0.00701±0.01	8.41±1.96	
0 V	Pd-O	0.16±0.02	2.12±0.08	0.00401±0.01	-5.00±1.98	0.00431
	Pd-Pd/Rh	1.43±0.23	2.66±0.02	0.00701±0.02	6.21±2.39	
	Pd-Mo	3.68±0.44	2.82±0.04	0.00701±0.01	4.21±5.91	
	Pd-Fe/Mn	1.08±0.20	2.91±0.06	0.00701±0.00	8.41±2.02	
-0.025 V	Pd-O	0.17±0.03	2.12±0.01	0.00401±0.01	-5.00±3.91	0.00321
	Pd-Pd/Rh	1.43±0.20	2.66±0.02	0.00701±0.01	7.37±1.45	
	Pd-Mo	3.68±0.21	2.82±0.04	0.00701±0.00	4.28±5.11	
	Pd-Fe/Mn	1.14±0.12	2.90±0.09	0.00701±0.02	8.41±0.65	
-0.05 V	Pd-O	0.24±0.02	2.12±0.02	0.00401±0.02	-5.00±3.87	0.00262
	Pd-Pd/Rh	1.43±0.25	2.66±0.03	0.00701±0.01	9.14±4.53	
	Pd-Mo	3.68±0.30	2.83±0.05	0.00701±0.01	5.01±8.18	
	Pd-Fe/Mn	1.43±0.20	2.92±0.05	0.00701±0.03	8.41±1.16	
-0.1 V	Pd-O	0.25±0.03	2.12±0.02	0.00401±0.01	-5.00±1.99	0.00435
	Pd-Pd/Rh	1.43±0.17	2.68±0.02	0.00701±0.02	6.61±7.77	
	Pd-Mo	3.68±0.16	2.81±0.04	0.00701±0.02	1.87±5.25	
	Pd-Fe/Mn	1.53±0.21	2.89±0.05	0.00701±0.02	8.41±5.79	

Supplementary Table 9. Model-fitted operando EXAFS spectra results for Pd in 0.5 M H₂SO₄.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Pd-O	0.17±0.16	2.12±0.03	0.00401±0.00	-5.00±5.39	0.00363
	Pd-Pd/Rh	1.43±0.19	2.65±0.04	0.00701±0.01	-6.35±9.00	
	Pd-Mo	3.68±0.39	2.77±0.03	0.00701±0.02	-3.17±5.51	
	Pd-Fe/Mn	1.00±0.19	2.96±0.04	0.00701±0.00	-2.42±7.83	
0 V	Pd-O	0.17±0.29	2.12±0.01	0.00401±0.00	-5.00±2.39	0.00296
	Pd-Pd/Rh	1.43±0.48	2.65±0.07	0.00701±0.02	-8.21±4.06	
	Pd-Mo	3.68±0.55	2.81±0.02	0.00701±0.02	-1.74±6.57	
	Pd-Fe/Mn	1.00±0.02	2.87±0.05	0.00701±0.00	8.31±7.17	
-0.025 V	Pd-O	0.17±0.23	2.12±0.01	0.00401±0.01	-5.00±6.92	0.00203
	Pd-Pd/Rh	1.43±0.20	2.63±0.05	0.00701±0.01	-11.22±9.05	
	Pd-Mo	3.68±0.35	2.81±0.03	0.00701±0.01	-0.95±4.78	
	Pd-Fe/Mn	1.00±0.09	2.83±0.05	0.00701±0.00	8.12±6.71	
-0.05 V	Pd-O	0.17±0.17	2.12±0.01	0.00401±0.00	-5.00±1.02	0.00337
	Pd-Pd/Rh	1.43±0.25	2.65±0.08	0.00701±0.00	-0.98±0.99	
	Pd-Mo	3.68±0.13	2.78±0.04	0.00701±0.02	-0.98±0.41	
	Pd-Fe/Mn	1.00±0.03	2.96±0.03	0.00701±0.01	12.66±1.11	
-0.1 V	Pd-O	0.17±0.32	2.12±0.00	0.00401±0.00	-5.00±3.31	0.00446
	Pd-Pd/Rh	1.43±0.21	2.55±0.03	0.00701±0.01	-8.406±2.71	
	Pd-Mo	3.68±0.45	2.82±0.05	0.00701±0.00	-1.921±3.12	
	Pd-Fe/Mn	1.00±0.10	2.89±0.02	0.00701±0.01	8.312±5.98	

Supplementary Table 10. Model-fitted operando EXAFS spectra results for Rh in 1.0 M KOH.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Rh-O	0.24±0.22	1.88±0.01	0.00623±0.00	0.00±2.91	0.00181
	Rh-Rh/Pd	2.14±0.15	2.53±0.00	0.00712±0.02	-2.34±1.06	
	Rh-Mo	4.83±0.14	2.71±0.00	0.00712±0.00	6.85±2.80	
	Rh-Fe/Mn	2.30±0.13	2.60±0.01	0.00712±0.00	8.77±0.67	
0 V	Rh-O	0.24±0.18	1.88±0.01	0.00623±0.00	0.00±0.95	0.00177
	Rh-Rh/Pd	2.14±0.12	2.53±0.00	0.00712±0.00	2.72±1.39	
	Rh-Mo	4.83±0.22	2.71±0.01	0.00712±0.00	7.41±2.88	
	Rh-Fe/Mn	2.30±0.20	2.60±0.03	0.00712±0.01	8.72±0.52	
-0.025 V	Rh-O	0.25±0.10	1.88±0.01	0.00623±0.01	0.00±0.46	0.00146
	Rh-Rh/Pd	2.15±0.16	2.52±0.00	0.00712±0.01	3.17±7.68	
	Rh-Mo	4.83±0.01	2.71±0.00	0.00712±0.00	7.63±1.91	
	Rh-Fe/Mn	2.30±0.09	2.60±0.02	0.00712±0.01	8.77±0.71	
-0.05 V	Rh-O	0.25±0.23	1.88±0.01	0.00623±0.00	0.00±2.67	0.00182
	Rh-Rh/Pd	2.15±0.17	2.52±0.00	0.00712±0.02	2.68±8.52	
	Rh-Mo	4.83±0.16	2.71±0.00	0.00712±0.01	7.38±2.12	
	Rh-Fe/Mn	2.30±0.14	2.61±0.03	0.00712±0.01	8.49±0.74	
-0.1 V	Rh-O	0.25±0.19	1.88±0.02	0.00623±0.00	0.00±5.06	0.00173
	Rh-Rh/Pd	2.15±0.11	2.52±0.00	0.00712±0.01	2.78±3.13	
	Rh-Mo	4.83±0.24	2.71±0.00	0.00712±0.00	7.55±0.78	
	Rh-Fe/Mn	2.30±0.01	2.61±0.00	0.00712±0.00	8.57±0.37	

Supplementary Table 11. Model-fitted operando EXAFS spectra results for Rh in 1.0 M PBS.

Sample	Path	CN	R (Å)	$\sigma^2(\text{Å}^2)$	E0	R-factor
OCP	Rh-O	0.12±0.01	1.88±0.05	0.00521±0.01	0.00±0.07	0.00929
	Rh-Rh/Pd	2.14±0.69	2.55±0.07	0.00712±0.00	-8.71±6.25	
	Rh-Mo	4.83±0.33	2.73±0.01	0.00712±0.01	7.83±0.93	
	Rh-Fe/Mn	2.30±0.52	2.60±0.06	0.00712±0.00	0.95±4.51	
0 V	Rh-O	0.12±0.02	1.88±0.05	0.00521±0.01	0.00±0.06	0.00249
	Rh-Rh/Pd	2.14±0.27	2.55±0.05	0.00712±0.00	-8.68±2.29	
	Rh-Mo	4.83±0.55	2.74±0.02	0.00712±0.00	8.67±0.38	
	Rh-Fe/Mn	2.30±0.45	2.60±0.04	0.00712±0.01	0.44±2.94	
-0.025 V	Rh-O	0.12±0.01	1.88±0.03	0.00521±0.00	0.00±0.03	0.00192
	Rh-Rh/Pd	2.15±0.57	2.56±0.02	0.00712±0.01	-9.34±2.22	
	Rh-Mo	4.83±0.55	2.74±0.03	0.00712±0.00	8.60±0.98	
	Rh-Fe/Mn	2.30±0.37	2.60±0.01	0.00712±0.01	-2.07±1.67	
-0.05 V	Rh-O	0.12±0.01	1.88±0.01	0.00521±0.01	0.00±0.04	0.00493
	Rh-Rh/Pd	2.15±0.39	2.54±0.03	0.00712±0.02	-6.71±2.99	
	Rh-Mo	4.83±0.43	2.74±0.02	0.00712±0.00	8.90±4.39	
	Rh-Fe/Mn	2.30±0.24	2.60±0.01	0.00712±0.01	1.55±0.48	
-0.1 V	Rh-O	0.12±0.01	1.88±0.04	0.00521±0.01	0.00±1.12	0.00527
	Rh-Rh/Pd	2.14±0.31	2.54±0.01	0.00712±0.01	-9.84±7.58	
	Rh-Mo	4.83±0.32	2.74±0.00	0.00712±0.00	8.79±2.21	
	Rh-Fe/Mn	2.30±0.25	2.60±0.01	0.00712±0.01	-0.25±5.72	

Supplementary Table 12. Model-fitted operando EXAFS spectra results for Rh in 0.5 M H₂SO₄.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Rh-O	0.25±0.17	1.88±0.01	0.00623±0.01	0.00±0.01	0.00518
	Rh-Rh/Pd	2.14±0.24	2.49±0.02	0.00712±0.02	-0.15±7.06	
	Rh-Mo	4.83±0.26	2.69±0.03	0.00712±0.00	4.70±9.28	
	Rh-Fe/Mn	2.30±0.26	2.62±0.02	0.00712±0.01	10.39±4.73	
0 V	Rh-O	0.25±0.21	1.88±0.01	0.00623±0.01	0.00±1.40	0.00572
	Rh-Rh/Pd	2.14±0.42	2.40±0.03	0.00712±0.00	-0.60±1.51	
	Rh-Mo	4.83±0.51	2.69±0.01	0.00712±0.00	4.07±7.56	
	Rh-Fe/Mn	2.30±0.43	2.62±0.03	0.00712±0.01	9.805±1.01	
-0.025 V	Rh-O	0.25±0.12	1.88±0.01	0.00623±0.00	0.00±2.09	0.00593
	Rh-Rh/Pd	2.15±0.22	2.50±0.00	0.00712±0.01	0.09±1.52	
	Rh-Mo	4.83±0.24	2.68±0.03	0.00712±0.02	4.14±9.80	
	Rh-Fe/Mn	2.30±0.23	2.62±0.01	0.00712±0.00	9.68±1.02	
-0.05 V	Rh-O	0.25±0.20	1.88±0.00	0.00623±0.00	0.00±3.99	0.00748
	Rh-Rh/Pd	2.15±0.24	2.50±0.02	0.00712±0.02	0.11±3.81	
	Rh-Mo	4.83±0.26	2.67±0.03	0.00712±0.01	3.84±9.90	
	Rh-Fe/Mn	2.30±0.25	2.62±0.01	0.00712±0.01	10.07±2.18	
-0.1 V	Rh-O	0.25±0.11	1.88±0.00	0.00623±0.00	0.00±3.31	0.00597
	Rh-Rh/Pd	2.15±0.22	2.49±0.02	0.00712±0.01	0.07±4.80	
	Rh-Mo	4.83±0.24	2.68±0.00	0.00712±0.01	3.40±1.60	
	Rh-Fe/Mn	2.30±0.23	2.62±0.01	0.00712±0.01	9.83±2.44	

Supplementary Table 13. Model-fitted operando Mn EXAFS spectra in 0.5 M H₂SO₄.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Mn-O	5.98±0.35	2.09±0.08	0.00585±0.004	-8.15±6.80	0.00166
0 V	Mn-O	5.91±0.36	2.07±0.08	0.00483±0.003	-8.95±8.20	0.00092
-0.025 V	Mn-O	5.78±0.85	2.10±0.07	0.00449±0.003	-6.29±-2.52	0.00092
-0.05 V	Mn-O	5.99±0.90	2.17±0.06	0.00559±0.003	-5.06±1.79	0.00063
-0.1 V	Mn-O	5.97±0.87	2.14±0.06	0.00676±0.003	-5.37±1.38	0.00125

Supplementary Table 14. Model-fitted operando Mn EXAFS spectra in 1.0 M KOH.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Mn-O	4.88±0.35	2.14±0.02	0.00771±0.001	-0.90±3.68	0.00104
0 V	Mn-O	5.09±0.56	2.15±0.03	0.00780±0.001	-0.08±5.52	0.00178
-0.025 V	Mn-O	5.16±0.61	2.15±0.03	0.00771±0.001	3.22±0.61	0.00258
-0.05 V	Mn-O	5.91±0.95	2.15±0.06	0.00762±0.001	-4.12±10.01	0.00252
-0.1 V	Mn-O	5.94±0.85	2.16±0.04	0.00762±0.001	6.01±5.67	0.00139

Supplementary Table 15. Model-fitted operando Mn EXAFS spectra in 1.0 M PBS.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Mn-O	2.35±0.19	2.22±0.02	0.00302±0.001	7.58±5.73	0.00207
0 V	Mn-O	2.44±0.19	2.20±0.03	0.00332±0.001	9.07±9.82	0.00197
-0.025 V	Mn-O	2.50±0.49	2.18±0.02	0.00302±0.001	15.28±2.27	0.00210
-0.05 V	Mn-O	2.52±0.49	2.19±0.03	0.00302±0.001	13.52±2.79	0.00214
-0.1 V	Mn-O	2.71±0.51	2.18±0.03	0.00302±0.001	13.44±2.93	0.00244

REVIEWER COMMENTS

Reviewer #2 (Remarks to the Author):

The authors have addressed the comments from the reviewer and the manuscript is ready for publication.

Reviewer #3 (Remarks to the Author):

Thank you for addressing the questions, you might want to consider including part of your answers in the main text:

Q1: thanks for clarifying, why not introduce this in the text?

Q3: I assume this text on XRD has now been removed from the text?

Q4: why not include this discussion in the main manuscript?

Q5: For XAFS to see any O contribution (that scatters also weakly) it has to be at a very distinct bond distances. This is ONLY the case when it is chemisorbed. I am afraid the reviewers for the cited publication here in ACS Energy Letters did not do a great job. Can you please rephrase the corresponding sentence in the main manuscript (and maybe add your argumentation that this chemisorbed O has little effect on the HER, in accordance with literature).

Line Q6: than add this text to the main document!

Line Q7: than add this to the main document.

Line Q8: Would the growth of Mn oxides not destroy your HEM?

The updated main manuscript is still not reflecting the basic standards of XAFS analysis and presentations of the XAFS results and thus I think it needs one serious go at it. Further comments based on reading the revised manuscript, especially the tables containing the fitting results in the supplementary texts should be addressed:

Line 90: please steer away from providing value, i.e. 'a daunting task'

Line 181: XPS results indicate a small fraction of PdO: is this not the result of surface oxidation during sample transport from synthesis conditions to the XPS sample chamber?

Line 391: These calculations were done by assuming all elements to be present in the metallic states. How would things change for Mn when it is oxidized (as found by XPS and XAS)?

Line 417: new text: please finish the sentence, an enhanced electron density on both Pd and Rh atoms

Line 440: I disagree: water from the electrolyte is never that ordered that you can see it with XAFS. If so, you are the first one to report. O results from chemisorbed O.

Lines 447-450: This is strange: you observe an increase in Pd-M contributions (an increase in peak height does not necessarily mean you have more neighbours: you need quantitative fitting results!) but assign this not to local coordination (as EXAFS probes) but an enhancement in charge density: this is NOT what EXAFS probes. Please change the argumentation here as this is incorrect. Quantitative fitting, Table S9, showed surprisingly absolutely no changes (with up to 2 digits behind the dot). First of all, that is impossible, we do not have that accuracy. Second of all, this does not support your argument.

Lines 459-460: Why not discuss these quantitative results, i.e. what did they show for the Pd-M contributions?

Line 461: How did you check? What did you learn from this?

Line 463: this is k-space, NOT with a capital.

Line 463: A Pd-O contribution does not indicate water dissociation *per se* but either PdOH at the surface or chemisorbed Pd-O.

Lines 471 and further: this suggests that Pd is as active site as Rh... in contrast to the statements you made following the DFT.

Line 474: and what happens to this adsorbed OH on Mn?

Line 488: what dynamic structure of the active sites did you show?? There were no dynamic XAFS measurements shown.

Line 528: give a reference to the software package used.

Supplementary S19: Pd clearly forms larger metallic particles according to the XANES spectra.

Table S7: It is ΔE_0 . Report only relevant digits for the CN, ΔE_0 and the DW factor. How is R-factor defined? Also, you have very unstable fits: probably too many parameters with 4 paths and a limited range: this is indicated by the huge error bars on the ΔE_0 . Also, somehow you show exactly the same numbers for the CN at different potentials (while before you indicated in lines 447-450) that there is an increase in intensity of this peak. Please explain, this does not make sense at all.

Response to Decision Letter

August 20, 2024

Journal: Nature Communications

Reference number: NCOMMS-23-58688B

Title: Operando Visualization of Multi-Site Synergistic H₂-Production Mechanisms on Sub-Nanometric High-Entropy Metallenes

Reviewer #2 (Remarks to the Author):

The authors have addressed the comments from the reviewer and the manuscript is ready for publication.

Response: We thank the reviewer for the positive comments and recommendation on the publication of this work. We also thanks for your previous constructive comments, which helped a lot for the improvement of this work.

Reviewer #3 (Remarks to the Author):

Thank you for addressing the questions, you might want to consider including part of your answers in the main text:

Q1: thanks for clarifying, why not introduce this in the text?

Response: Thanks for your suggestion. We have added an explanation of the “challenge” in the line 76 of the text.

Changes to the main text:

Line 76: Lamentedly, different metallic elements differ in size, crystal configuration, and electronegativity, resulting in varying degrees of lattice mismatch between them, which is not conducive to the HEA formation. Therefore, most of the reported HEAs are still confined to nanoparticles and the construction of sub-nanometric 2D HEA materials are scarce and challenging²⁸.

Q3: I assume this text on XRD has now been removed from the text?

Response: Thanks for your advice. We agree with you that the absence of other phases in XRD does not fully prove the successful preparation of HEAs and modified the XRD analysis. In this text, we objectively described and analyzed the results of the XRD spectrum and did not assume that this result necessarily indicates the formation of HEA. XRD is a widely used technique for characterizing nanomaterials including HEAs reported so far [Nat. Commun. 14, 4182 (2023); Nat

Commun 12, 6261 (2021); J. Am. Chem. Soc. 144, 10582-10590 (2022)]. We think it can be retained, as it can provide some useful information such as the *fcc* configuration and lattice distortion of PdRhMoFeMn HEMs, which is described in the line 131 of the text.

Changes to the main text:

Line 131: Additionally, the X-ray diffraction (XRD) pattern in Fig. 2d shows that PdRhMoFeMn HEMs possess a face-centered cubic (*fcc*) configuration without phase segregation, which is analogous to that of pure Pd. The weakening and broadening of XRD peaks could be attributable to the lattice distortion originating from the interposition of Mn, Fe, Rh, and Mo atoms.

Q4: why not include this discussion in the main manuscript?

Response: Thanks for your suggestion. We have included this discussion in the main manuscript.

Changes to the main text:

Line 166: In addition, the extended X-ray absorption fine structure (EXAFS) spectra of HEMs show an obvious prominent peak at ~ 2.75 Å for Pd-M (Fig. 3b) and ~ 2.75 Å for Rh-M (Fig. 3d), respectively. Due to the thinness of the material, lower coordination numbers and a homogeneous distribution of metal atoms, it is indeed possible to observe Rh-Rh and Pd-Pd neighbors. Moreover, Pd-M and Rh-M are slightly distinct from the Pd-Pd and Rh-Rh bonds in Pd and Rh references. This phenomenon results from small changes in the coordination environment caused by the presence of other smaller atoms (Mo, Fe, and Mn) around the relatively large Pd and Rh atoms. Therefore, M can be Pd, Rh, Mo, Fe, or Mn.

Q5: For XAFS to see any O contribution (that scatters also weakly) it has to be at a very distinct bond distances. This is ONLY the case when it is chemisorbed. I am afraid the reviewers for the cited publication here in ACS Energy Letters did not do a great job. Can you please rephrase the corresponding sentence in the main manuscript (and maybe add your argumentation that this chemisorbed O has little effect on the HER, in accordance with literature).

Response: Thanks for your suggestion. We need to clarify that the observed O results are due to the chemisorbed oxygen. In addition, we have rephrased the corresponding sentence and added our argumentation that this chemisorbed O has little effect on the HER in the main manuscript.

Changes to the main text:

Line 199: Specifically, the HER activity of RhO₂ and PdO is much lower than that of PdRhMoFeMn HEMs (Supplementary Fig. 7), which indicates the effects of these trace amounts of metal oxygen species on the HER mechanism and performance are minimal, which are generally

ignorable in reported literature^{42,51,52}.

Q6: than add this text to the main document!

Response: Thanks for your suggestion. We have added this text in the main manuscript.

Changes to the main text:

Line 195: Due to the exposure of under-coordinated corner atoms and edge atoms with stronger oxyphilic nature in ultra-thin HEMs to air, the trace metal oxygen species on the catalyst surface are formed, which is a common phenomenon in the reported literature^{16,26,50}.

Q7: than add this to the main document.

Response: Thanks for your suggestion. We have added this text in the main manuscript.

Changes to the main text:

Line 140: The difference between the initial feed ratio and the ratio of elements in the obtained HEMs is due to the difference in the reduction difficulty of various metal precursors^{40,41}.

Q8: Would the growth of Mn oxides not destroy your HEM?

Response: Thanks for your question. The number of Mn-related oxides formed during the HER process is extremely small and exists on the catalyst surface, so its effect on the structure of HEMs is minimal and does not destroy HEMs. The TEM, XRD, ICP-OES and XANES results after the stability test in Supplementary Fig. 19 and 20 and the corresponding analysis in line 273-283 further showed that the changes in the morphology, crystal structure and electronic structure of HEMs were very small, which also proved that HEMs were not destroyed during the reaction. We have included this discussion in the main manuscript.

Changes to the main text:

Line 485: Importantly, the above-mentioned relevant characterizations after stability tests indicate that the formation of trace amounts of Mn-related oxides has little effect on the morphology, crystal structure, and electronic structure of HEMs.

The updated main manuscript is still not reflecting the basic standards of XAFS analysis and presentations of the XAFS results and thus I think it needs one serious go at it. Further comments based on reading the revised manuscript, especially the tables containing the fitting results in the supplementary texts should be addressed:

Response: We thank the reviewer for your professional advice, which is of great significance to the improvement of our work. We understand that this is the last round of opportunities provided by the

editor to address your concerns. Based on these additional comments, we have treated seriously to your comments, conducted a series of necessary supplemental experiments and analysis, and tried our best to address your comments. All changes have been highlighted in the revised manuscript by formatting the text in Yellow color. Detailed lists of revisions are listed below:

Q1. Line 90: please steer away from providing value, i.e. ‘a daunting task’.

Response: Thanks for your suggestion here. We carefully checked the inappropriate words in the main manuscript and made corrections accordingly.

Changes to the main text:

Line 92: As an equally crucial catalyst system, it remains to be explored to gain atomistic-level insight into active site dynamics and interaction mechanisms for HEAs with tanglesome atomic arrangements and multiple elements of similar electron contrasts under realistic catalytic conditions³⁹.

Q2. Line 181: XPS results indicate a small fraction of PdO: is this not the result of surface oxidation during sample transport from synthesis conditions to the XPS sample chamber?

Response: Thanks for your question. When the prepared HEMs are exposed to air, a small amount of under-coordinated corner atoms and edge atoms with stronger oxyphilic nature on the catalyst surface will be oxidized. This phenomenon is very common in the reported literature [Nature 574, 81-85 (2019); ACS Nano 16, 522-532 (2022)]. Even on the surface of Pd foil, there will be a small amount of oxidized Pd atoms. In the reported literature, researchers usually focus on the main material and ignore the small amount of surface metal oxide species that have little impact on the research results [Nat. Commun. 13, 2662 (2022); Nat. Commun. 15, 359 (2024); Adv. Mater. 36, 2309715 (2023)]. During sample transport from synthesis conditions to the XPS sample chamber, the Pd atoms on the surface of HEMs may be slightly oxidized. However, Pd in HEMs is mainly in its metallic state, which has little effect on our research conclusions. We have included this discussion in the main manuscript.

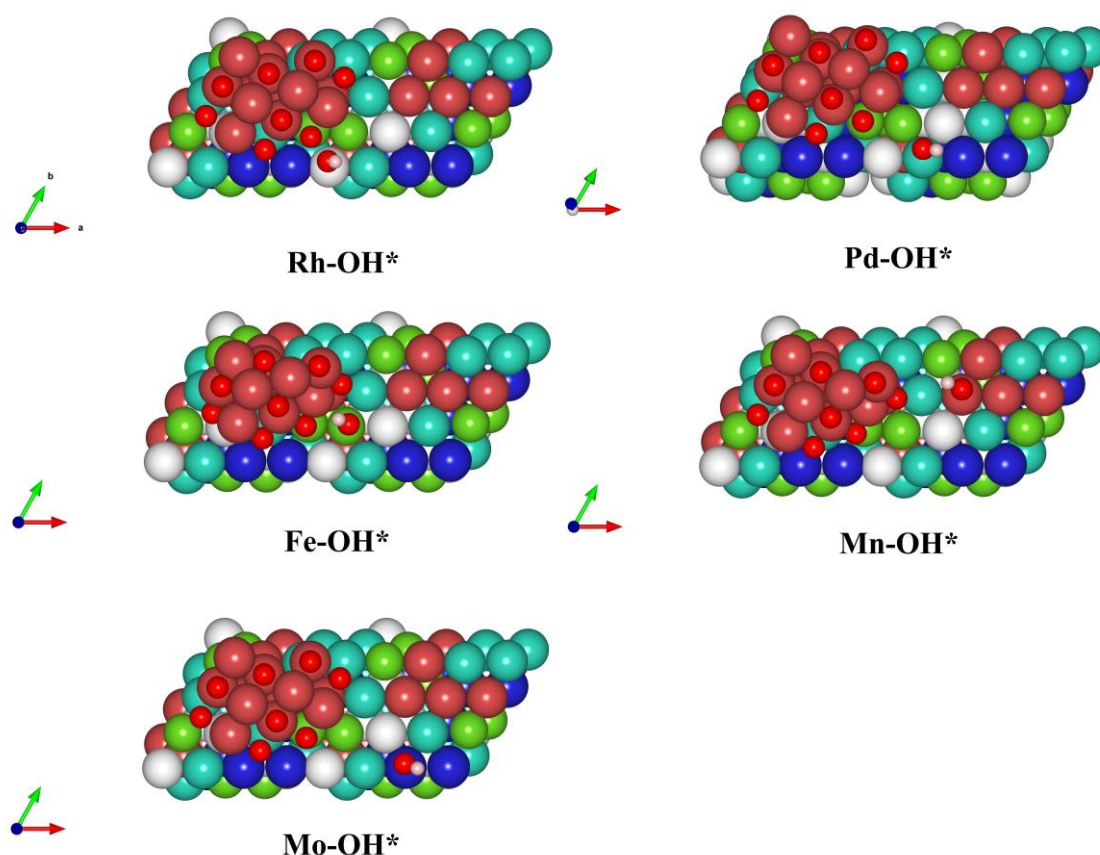
Changes to the main text:

Line 195: Due to the exposure of under-coordinated corner atoms and edge atoms with stronger oxyphilic nature in ultra-thin HEMs to air, the trace metal oxygen species on the catalyst surface are formed, which is a common phenomenon in the reported literature^{16,26,50}. Specifically, the HER activity of RhO₂ and PdO is much lower than that of PdRhMoFeMn HEMs (Supplementary Fig. 7), which indicates the effects of these trace amounts of metal oxygen species on the HER mechanism

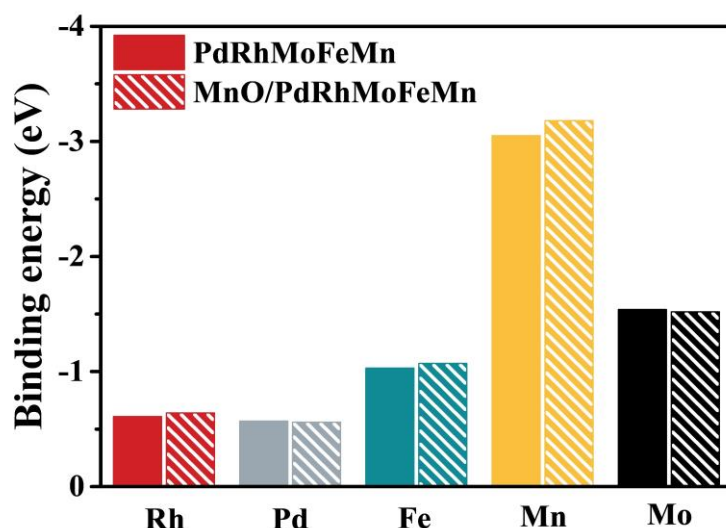
and performance are minimal, which are generally ignorable in reported literature^{42,51,52}.

Q3. Line 391: These calculations were done by assuming all elements to be present in the metallic states. How would things change for Mn when it is oxidized (as found by XPS and XAS)?

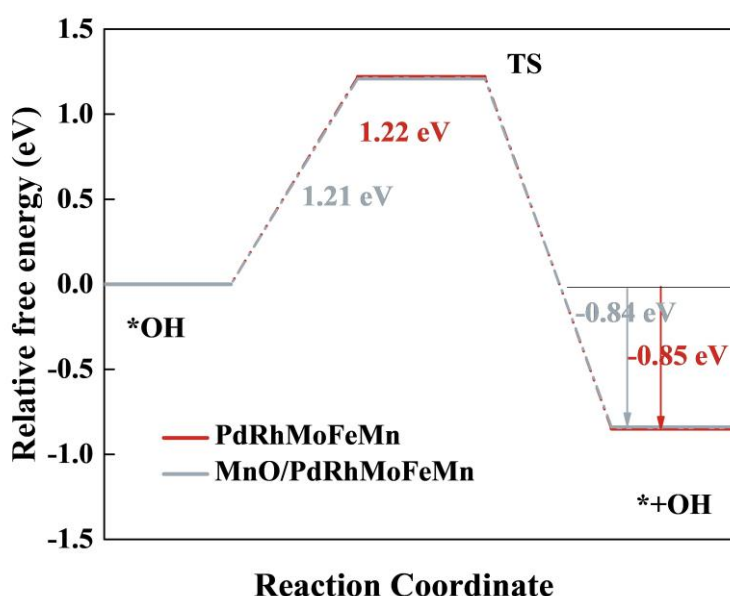
Response: Thank the reviewer for the valuable suggestion. Based on your suggestion, we have added the calculation of the OH* adsorption and desorption energies for a homogeneous HEM with MnO clusters (MnO/PdRhMoFeMn HEMs). Supplementary Fig. 61 shows the atomic configurations of different sites in MnO/PdRhMoFeMn HEMs during the OH* adsorption process. As displayed in Supplementary Fig. 62, the formation of a small amount of MnO on the HEM surface has little effect on the adsorption of OH* at various sites in HEMs. Among them, the Mn site in MnO/PdRhMoFeMn HEMs still shows the strongest adsorption capacity for OH* (-3.18 eV), which is close to that of PdRhMoFeMn HEMs (-3.05 eV). In addition, the OH* desorption energy of MnO/PdRhMoFeMn HEMs (-0.84 eV) is similar to that of PdRhMoFeMn HEMs (-0.85 eV) (Supplementary Fig. 63). These results show that the formation of trace oxide clusters during the reaction has minimal impact on the OH adsorption and desorption at the Mn site. We have included this discussion in the main manuscript.



Supplementary Fig. 61 The atomic configurations of different sites in MnO/ PdRhMoFeMn HEMs during the OH* adsorption process.



Supplementary Fig. 62 The adsorption energy of hydroxide at different sites for MnO/PdRhMoFeMn HEMs.



Supplementary Fig. 63 The desorption energy of hydroxide at different sites for PdRhMoFeMn and MnO/PdRhMoFeMn HEMs.

Changes to the main text:

Line 487: DFT calculations also show that the ΔG_{H^*} , OH^* adsorption energy, and OH^* desorption energy of MnO/ PdRhMoFeMn HEMs is -0.13, -3.18, and -0.84 eV, respectively, which is close to that of PdRhMoFeMn HEMs (-0.132, -3.05, and -0.85 eV) (Supplementary Figs. 59-63). These results indicate that the formation of trace oxide clusters during the reaction has minimal impact on its HER performance, which is consistent with its excellent HER stability.

Q4. Line 417: new text: please finish the sentence, an enhanced electron density on both Pd and Rh atoms.

Response: Thank the reviewer for your kind reminder. According to your comments, we have finished the sentence.

Changes to the main text:

Line 430: The XANES spectra in Fig. 6c,d demonstrate a reduction in the white line intensity of both Pd and Rh, indicating an enhanced electron density on both Pd and Rh atoms upon the application of a reduction potential.

Q5. Line 440: I disagree: water from the electrolyte is never that ordered that you can see it with XAFS. If so, you are the first one to report. O results from chemisorbed O.

Response: Thanks for your professional comments. We need to clarify that the observed O results are due to chemisorbed oxygen. Operando observations indicate an increase in the Metal-O peak, signifying the presence of chemisorbed oxygen. We have made corresponding corrections in the revised manuscript.

Changes to the main text:

Line 483: Chemisorbed oxygen-related species was observed in Pd, Rh, and Mn, but only Mn formed obvious oxides in the end.

Q6. Lines 447-450: This is strange: you observe an increase in Pd-M contributions (an increase in peak height does not necessarily mean you have more neighbours: you need quantitative fitting results!) but assign this not to local coordination (as EXAFS probes) but an enhancement in charge density: this is NOT what EXAFS probes. Please change the argumentation here as this is incorrect. Quantitative fitting, Table S9, showed surprisingly absolutely no changes (with up to 2 digits behind the dot). First of all, that is impossible, we do not have that accuracy. Second of all, this does not support your argument.

Response: Thank you for your detailed review. The increase in Pd-M contributions is likely influenced by a higher coordination number and a lower Debye-Waller factor. Consequently, we included the fitting results from Table S10 into the discussion, determining that the primary factor is the coordination number. Therefore, attributing the results to an enhancement in charge density is inappropriate. Instead, we believe that structural reconstruction has occurred.

Regarding the fitting method, we initially fitted from OCP to determine each parameter. After fitting at OCP spectra, we use the replace spectra function to fit each subsequent potential. However, fixing the coordination number during fitting caused the coordination numbers to be identical, which was problematic. To address this, we decided to refit the spectra without fixing the

coordination number. The fitted data is presented in Table S7-15.

Changes to the main text:

Line 466: At the same time, the gradual increase in the coordination numbers of Pd-M implies the occurred structural reconstruction.

Q7. Lines 459-460: Why not discuss these quantitative results, i.e. what did they show for the Pd-M contributions?

Response: Thank you for your review comments. We have updated the fitting results and included specific descriptions for Supplementary Figs. 54-56 and Supplementary Tables 7-15 in the line 451-474 of the revised manuscript. For instance, Supplementary Tables 10 and 11 demonstrate the almost unchanged coordination environment of Pd and Rh under acidic conditions. Supplementary Fig. 56b and Supplementary Table 12 indicate that the gradual increase in the coordination numbers of Pd-M implies the occurred structural reconstruction in alkaline solutions.

Q8. Line 461: How did you check? What did you learn from this?

Response: Thank you for the thorough review. The description was indeed inappropriate. We have removed the entire description in Line 461. The in situ Pd and Rh spectra were used to probe the two active sites at the atomic level to help understand the reaction mechanism. We have now updated the manuscript with a detailed description (Line 457-483).

Q9. Line 463: this is k-space, NOT with a capital.

Response: We apologize for this error. We have revised it in line 479 of the main manuscript.

Q10. Line 463: A Pd-O contribution does not indicate water dissociation perse but either PdOH at the surface or chemisorbed Pd-O.

Response: Thanks for your professional comments. We fully agree that the direct observation of the water dissociation step in HER is quite challenging. This process is primarily inferred by the detection of chemisorbed oxygen species combined with the above theoretical calculations and Tafel slope analysis. We apologize for the inconvenience this inappropriate description has caused you and have made corresponding corrections.

Changes to the main text:

Line 478: Simultaneously, based on Supplementary Fig. 58 k-space spectra, where a slight contribution from Pd-O is observed between 3-6 Å⁻¹, indicating the trend of chemisorbed oxygen species on Pd sites, and Pd-O fitting was also conducted to further understand the HER mechanisms. This result, combined with the above theoretical calculations and Tafel slope analysis, suggests a

possible water dissociation process on Pd sites.

Q11. Lines 471 and further: this suggests that Pd is an as active site as Rh... in contrast to the statements you made following the DFT.

Response: Thank the reviewer for your question. In line 471, we explained that under alkaline conditions, Pd is the site of water molecular dissociation, and then the generated H intermediate species is transferred to the Rh site to produce H₂. Therefore, both Pd and Rh are active sites. In the DFT section, in the acidic electrolyte, Rh is the only site for the adsorption of H* intermediates and the H₂ generation since no water dissociation step is involved (line 366-369). However, under alkaline conditions, Fig. 5g and 5h indicate that Pd is the water adsorption and dissociation site (line 398-403). Subsequently, the H* intermediate species produced by water dissociation at the Pd site is transferred to the Rh site to generate H₂ (line 407). Therefore, DFT also shows that Pd and Rh are active sites under alkaline conditions, which is consistent with the results of in-situ XAS. We apologize for any confusion this may have caused you.

Q12. Line 474: and what happens to this adsorbed OH on Mn?

Response: Thank the reviewer for your question. The adsorption of OH produced by water dissociation on Mn sites will destabilize bonds in the water molecule, reducing the energy barrier for water dissociation [Nat. Energy 4, 107-114 (2019)]. Moreover, the adsorption of OH on Mn sites would release more Pd sites to accelerate the water dissociation step. This conclusion is corroborated by the reduced water dissociation barrier revealed by DFT and the enhanced HER kinetics revealed by the Tafel slope. Subsequently, the OH adsorbed on the Mn sites is desorbed into the electrolyte.

Changes to the main text:

Line 501: Simultaneously, the formed OH intermediates are absorbed onto the Mn sites, which can destabilize bonds in the water molecule and release more Pd sites to accelerate the water dissociation process⁵⁷. Subsequently, the OH adsorbed on the Mn sites is desorbed into the electrolyte.

Q13. Line 488: what dynamic structure of the active sites did you show?? There were no dynamic XAFS measurements shown.

Response: Indeed, we have presented a simplified version of the hydrogen evolution reaction (HER) steps, excluding the dynamic structure during process. The operando analysis primarily focuses on atomically probing the active sites of Pd, Rh, and Mn. Therefore, to avoid any potential confusion,

we will remove the sentence regarding dynamic changes.

Changes to the main text:

Line 518: More importantly, operando XAS verified the ability of HEMs to stabilize multiple intermediates at different active centers, and atomically observed the active sites of Pd, Rh, and Mn and the mechanisms of multi-site synergy in various electrolytes during the electrocatalytic HER processes.

Q14. Line 528: give a reference to the software package used.

Response: Thank you for your review comments. We have added the relevant citations to the manuscript. [Ravel B., Newville M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 2005, 12 (4), 537-541]. Regarding the EXAFS]

Changes to the main text:

Line 560: EXAFS fitting was performed using the ARTEMIS module of the Demeter software packages based on the reported literature⁵⁹, and the details are presented in the Supplementary Information.

Q15. Supplementary S19: Pd clearly forms larger metallic particles according to the XANES spectra.

Response: Indeed, slight structural reconstruction occurs after 10,000 CV cycles. Supplementary Fig. 20 demonstrates that there are no significant changes in the XANES spectra of each element after these cycles. However, some metallic Pd sites might appear (Supplementary Fig. 20a), though they have a relatively minor effect on performance, proved by almost unchanged HER activity after 10,000 cycles (Fig. 4d). We have added this description in the revised manuscript.

Changes to the main text:

Line 279: Supplementary Fig. 20 also shows that after 10,000 cycles, there are no significant changes observed in the XANES spectra of each element. However, some metallic Pd sites may appear (Supplementary Fig. 20a), with a relatively small impact on the performance of PdRhMoFeMn HEMs, which is proved by almost unchanged HER activity after 10,000 cycles (Fig. 4d).

Q16. Table S7: It is ΔE_0 . Report only relevant digits for the CN, ΔE_0 and the DW factor. How is R-factor defined? Also, you have very unstable fits: probably too many parameters with 4 paths and a limited range: this is indicated by the huge error bars on the ΔE_0 . Also, somehow

you show exactly the same numbers for the CN at different potentials (while before you indicated in lines 447-450) that there is an increase in intensity of this peak. Please explain, this does not make sense at all.

Response: Thank you for the reviewer's comments. The R-factor represents the discrepancy between the theoretical and experimental spectra, with smaller values indicating better fits, ideally below 0.02. Also, we have revised the relevant digits based on the reference [Nat. Commun. 15, 6174 (2024)] and updated Tables S7-S15 accordingly. Regarding the fitting method, we initially fitted from OCP to determine the coordination number, followed by employing the replace spectra function. For spectra showing no changes, we fixed the coordination number before fitting, which might have resulted in the appearance of no changes. Fitting each spectrum with fixed coordination number and DW factor did present some issues, prompting us to refit the spectra for Pd and Rh. We have now updated the fitting results in Table S7-S15 and Supplementary Fig. 55-57.

Finally, we hope that all your concerns have been addressed by this final round of responses. Thank you very much again for your attention and kindness to improve our work.

Supplementary Table 7. Model-fitted operando Mn EXAFS spectra in 0.5 M H₂SO₄.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Mn-O	6.0±0.3	2.09±0.08	5.8±0.1	-8.1±6.8	0.001
0 V	Mn-O	5.9±0.4	2.07±0.08	4.8±0.1	-9.0±8.2	0.001
-0.025 V	Mn-O	5.8±0.9	2.10±0.07	4.5±0.1	-6.2±-2.5	0.001
-0.05 V	Mn-O	6.0±0.9	2.17±0.06	5.6±0.1	-5.1±1.8	0.001
-0.1 V	Mn-O	6.0±0.9	2.14±0.06	6.8±0.1	-5.3±1.4	0.001

Supplementary Table 8. Model-fitted operando Mn EXAFS spectra in 1.0 M KOH.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Mn-O	4.9±0.4	2.14±0.02	7.7±0.1	-0.9±3.7	0.001
0 V	Mn-O	5.1±0.6	2.15±0.03	7.8±0.1	-0.1±5.5	0.002
-0.025 V	Mn-O	5.2±0.6	2.15±0.03	7.7±0.1	3.2±0.6	0.003
-0.05 V	Mn-O	5.9±1.0	2.15±0.06	7.6±0.1	-4.1±10.0	0.003
-0.1 V	Mn-O	5.9±0.9	2.16±0.04	7.6±0.1	6.0±5.7	0.001

Supplementary Table 9. Model-fitted operando Mn EXAFS spectra in 1.0 M PBS.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Mn-O	2.4±0.2	2.22±0.02	3.0±0.1	7.6±5.7	0.002
0 V	Mn-O	2.4±0.2	2.20±0.03	3.3±0.1	9.1±9.8	0.002
-0.025 V	Mn-O	2.5±0.5	2.18±0.02	3.0±0.1	15.2±2.2	0.002
-0.05 V	Mn-O	2.5±0.5	2.19±0.03	3.0±0.1	13.5±2.8	0.002
-0.1 V	Mn-O	2.7±0.5	2.18±0.03	3.0±0.1	13.4±2.9	0.002

Supplementary Table 10. Model-fitted operando EXAFS spectra results for Pd in 0.5 M H₂SO₄.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Pd-O	0.2±0.1	2.12±0.03	4.0±0.1	-5.0±5.4	0.003
	Pd-Pd/Rh	1.3±0.2	2.65±0.04	7.7±0.1	-6.4±9.0	
	Pd-Mo	3.7±0.4	2.77±0.03	7.2±0.1	-3.2±5.5	
	Pd-Fe/Mn	1.2±0.2	2.96±0.04	7.0±0.1	-2.4±7.8	
0 V	Pd-O	0.2±0.1	2.12±0.01	4.1±0.1	-5.0±2.4	0.003
	Pd-Pd/Rh	1.4±0.5	2.65±0.07	7.0±0.1	-8.2±4.1	
	Pd-Mo	3.8±0.6	2.81±0.02	7.1±0.1	-1.7±6.6	
	Pd-Fe/Mn	1.0±0.1	2.87±0.05	7.5±0.1	8.3±7.2	
-0.025 V	Pd-O	0.2±0.1	2.12±0.01	4.0±0.1	-5.0±6.9	0.002
	Pd-Pd/Rh	1.4±0.2	2.63±0.05	6.9±0.1	-11.2±9.1	
	Pd-Mo	3.7±0.4	2.81±0.03	6.7±0.1	-1±4.8	
	Pd-Fe/Mn	1.1±0.1	2.83±0.05	7.1±0.1	8.1±6.7	
-0.05 V	Pd-O	0.2±0.1	2.12±0.01	3.9±0.1	-5.0±1.0	0.003
	Pd-Pd/Rh	1.4±0.3	2.65±0.08	6.8±0.1	-1.0±1.0	
	Pd-Mo	3.7±0.1	2.78±0.04	7.2±0.1	-1.0±0.4	
	Pd-Fe/Mn	1.1±0.1	2.96±0.03	7.3±0.1	12.7±1.1	
-0.1 V	Pd-O	0.2±0.1	2.12±0.01	4.2±0.1	-5.0±3.3	0.004
	Pd-Pd/Rh	1.4±0.2	2.55±0.03	7.1±0.1	-8.4±2.7	
	Pd-Mo	3.6±0.5	2.82±0.05	7.2±0.1	-1.9±3.1	
	Pd-Fe/Mn	1.1±0.1	2.89±0.02	7.4±0.1	8.3±6.0	

Supplementary Table 11. Model-fitted operando EXAFS spectra results for Rh in 0.5 M H₂SO₄.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Rh-O	0.3±0.2	1.88±0.01	6.2±0.1	-1.7±0.1	0.005
	Rh-Rh/Pd	2.1±0.2	2.49±0.02	7.1±0.1	-0.2±7.1	
	Rh-Mo	4.7±0.3	2.69±0.03	7.2±0.1	4.7±9.3	
	Rh-Fe/Mn	2.3±0.3	2.62±0.02	7.1±0.1	6.4±4.7	
0 V	Rh-O	0.3±0.2	1.88±0.01	5.6±0.1	-0.5±1.4	0.006
	Rh-Rh/Pd	2.1±0.4	2.40±0.03	7.2±0.1	-0.6±1.5	
	Rh-Mo	4.8±0.5	2.69±0.01	7.1±0.1	4.1±7.6	
	Rh-Fe/Mn	2.3±0.4	2.62±0.03	7.4±0.1	7.1±1.0	
-0.025 V	Rh-O	0.3±0.1	1.88±0.01	6.1±0.1	0.5±2.1	0.006
	Rh-Rh/Pd	2.2±0.2	2.50±0.01	7.1±0.1	0.1±1.5	
	Rh-Mo	4.9±0.2	2.68±0.03	7.0±0.1	4.1±9.8	
	Rh-Fe/Mn	2.2±0.2	2.62±0.01	7.1±0.1	6.7±1.0	
-0.05 V	Rh-O	0.3±0.2	1.88±0.01	6.2±0.1	0.7±4.0	0.007
	Rh-Rh/Pd	2.3±0.2	2.50±0.02	7.1±0.1	0.1±3.8	
	Rh-Mo	4.7±0.3	2.67±0.03	7.1±0.1	3.8±9.9	
	Rh-Fe/Mn	2.2±0.3	2.62±0.01	7.4±0.1	5.1±2.1	
-0.1 V	Rh-O	0.3±0.1	1.88±0.01	6.3±0.1	-1.2±3.3	0.006
	Rh-Rh/Pd	2.1±0.2	2.49±0.02	7.1±0.1	0.1±4.8	
	Rh-Mo	4.8±0.2	2.68±0.01	7.4±0.1	3.4±1.6	
	Rh-Fe/Mn	2.3±0.2	2.62±0.01	7.0±0.1	3.8±2.4	

Supplementary Table 12. Model-fitted operando EXAFS spectra results for Pd in 1.0 M KOH.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Pd-O	0.2±0.1	2.12±0.01	4.0±0.1	-5.0±2.5	0.004
	Pd-Pd/Rh	1.4±0.2	2.66±0.03	7.0±0.1	1.8±8.5	
	Pd-Mo	3.7±0.2	2.81±0.04	7.0±0.1	0.6±4.4	
	Pd-Fe/Mn	1.0±0.1	2.93±0.01	7.1±0.1	5.3±1.7	
0 V	Pd-O	0.4±0.1	2.12±0.02	3.6±0.1	-5.0±6.0	0.003
	Pd-Pd/Rh	1.5±0.2	2.56±0.08	6.6±0.1	0.7±0.3	
	Pd-Mo	3.7±0.2	2.78±0.02	6.9±0.1	0.2±3.5	
	Pd-Fe/Mn	1.1±0.1	2.96±0.02	7.1±0.1	3.2±1.1	
-0.025 V	Pd-O	0.5±0.1	2.12±0.03	4.2±0.1	-4.4±6.3	0.007
	Pd-Pd/Rh	1.5±0.1	2.56±0.01	7.0±0.1	0.5±3.8	
	Pd-Mo	3.8±0.5	2.78±0.04	7.4±0.1	0.1±6.1	
	Pd-Fe/Mn	1.2±0.1	2.96±0.02	7.2±0.1	3.3±0.8	
-0.05 V	Pd-O	0.6±0.1	2.12±0.02	5.1±0.1	-2.8±2.2	0.005
	Pd-Pd/Rh	1.5±0.3	2.66±0.03	7.0±0.1	3.0±0.0	
	Pd-Mo	3.9±0.4	2.82±0.02	7.1±0.1	0.2±5.8	
	Pd-Fe/Mn	1.4±0.1	2.91±0.01	7.3±0.1	2.3±2.5	
-0.1 V	Pd-O	0.7±0.1	2.12±0.01	6.1±0.1	-5.7±4.1	0.004
	Pd-Pd/Rh	1.5±0.1	2.68±0.05	7.0±0.1	3.4±9.4	
	Pd-Mo	3.9±0.5	2.82±0.04	7.6±0.1	1.0±6.9	
	Pd-Fe/Mn	1.5±0.1	2.93±0.01	6.5±0.1	4.3±7.2	

Supplementary Table 13. Model-fitted operando EXAFS spectra results for Rh in 1.0 M KOH.

Sample	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{\AA}^2)$	ΔE_0 (eV)	R-factor
OCP	Rh-O	0.2±0.1	1.88±0.01	6.2±0.1	0.0±2.9	0.002
	Rh-Rh/Pd	2.1±0.2	2.53±0.01	7.1±0.1	-2.3±1.1	
	Rh-Mo	4.8±0.1	2.71±0.01	7.0±0.1	6.9±2.8	
	Rh-Fe/Mn	2.3±0.1	2.60±0.01	7.1±0.1	8.8±0.7	
0 V	Rh-O	0.2±0.1	1.88±0.01	6.2±0.1	0.0±1.0	0.002
	Rh-Rh/Pd	2.2±0.1	2.53±0.01	7.1±0.1	2.7±1.4	
	Rh-Mo	4.7±0.2	2.71±0.01	7.1±0.1	7.4±2.9	
	Rh-Fe/Mn	2.4±0.2	2.60±0.03	7.0±0.1	8.7±0.5	
-0.025 V	Rh-O	0.3±0.1	1.88±0.01	6.2±0.1	2.2±0.5	0.001
	Rh-Rh/Pd	2.1±0.2	2.52±0.01	7.1±0.1	3.2±7.7	
	Rh-Mo	4.8±0.1	2.71±0.01	7.2±0.1	7.6±2.0	
	Rh-Fe/Mn	2.3±0.1	2.60±0.02	7.0±0.1	8.8±0.7	
-0.05 V	Rh-O	0.3±0.1	1.88±0.01	6.2±0.1	-0.2±2.7	0.001
	Rh-Rh/Pd	2.2±0.2	2.52±0.01	7.1±0.1	2.7±8.5	
	Rh-Mo	4.8±0.2	2.71±0.01	7.3±0.1	7.4±2.1	
	Rh-Fe/Mn	2.3±0.1	2.61±0.03	7.0±0.1	8.5±0.7	
-0.1 V	Rh-O	0.3±0.2	1.88±0.02	6.2±0.1	-0.2±5.1	0.001
	Rh-Rh/Pd	2.1±0.1	2.52±0.01	7.1±0.1	2.8±3.1	
	Rh-Mo	4.7±0.2	2.71±0.01	7.1±0.1	7.6±0.8	
	Rh-Fe/Mn	2.4±0.1	2.61±0.01	7.0±0.1	8.6±0.4	

Supplementary Table 14. Model-fitted operando EXAFS spectra results for Pd in 1.0 M PBS.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Pd-O	0.2±0.1	2.12±0.02	4.0±0.1	-2.0±1.0	0.003
	Pd-Pd/Rh	1.5±0.1	2.67±0.03	6.9±0.1	7.2±3.7	
	Pd-Mo	3.6±0.6	2.82±0.03	6.7±0.1	4.0±0.6	
	Pd-Fe/Mn	0.9±0.1	2.89±0.03	7.1±0.1	8.4±2.0	
0 V	Pd-O	0.2±0.1	2.12±0.08	4.1±0.1	-1.3±2.0	0.004
	Pd-Pd/Rh	1.5±0.2	2.66±0.02	7.0±0.1	6.2±2.4	
	Pd-Mo	3.7±0.4	2.82±0.04	7.2±0.1	4.2±6.0	
	Pd-Fe/Mn	1.1±0.2	2.91±0.06	6.5±0.1	8.4±2.0	
-0.025 V	Pd-O	0.2±0.1	2.12±0.01	4.1±0.1	3.7±3.9	0.003
	Pd-Pd/Rh	1.5±0.2	2.66±0.02	7.0±0.1	7.4±1.5	
	Pd-Mo	3.8±0.2	2.82±0.04	7.2±0.1	4.3±5.1	
	Pd-Fe/Mn	1.2±0.1	2.90±0.09	7.0±0.1	8.4±0.7	
-0.05 V	Pd-O	0.2±0.1	2.12±0.02	4.1±0.1	-2.1±3.9	0.002
	Pd-Pd/Rh	1.6±0.3	2.66±0.03	7.0±0.1	9.1±4.5	
	Pd-Mo	3.8±0.3	2.83±0.05	7.1±0.1	5.0±8.2	
	Pd-Fe/Mn	1.4±0.2	2.92±0.05	7.2±0.1	8.4±1.2	
-0.1 V	Pd-O	0.3±0.1	2.12±0.02	4.1±0.1	-3.3±2.0	0.004
	Pd-Pd/Rh	1.6±0.2	2.68±0.02	7.2±0.1	6.6±7.8	
	Pd-Mo	3.8±0.2	2.81±0.04	7.3±0.1	1.9±5.3	
	Pd-Fe/Mn	1.4±0.2	2.89±0.05	7.4±0.1	8.4±5.8	

Supplementary Table 15. Model-fitted operando EXAFS spectra results for Rh in 1.0 M PBS.

Sample	Path	CN	R (Å)	$\sigma^2(\text{\AA}^2)$	E0	R-factor
OCP	Rh-O	0.2±0.1	1.88±0.05	5.3±0.1	0.5±0.7	0.01
	Rh-Rh/Pd	2.0±0.7	2.55±0.07	7.1±0.1	-3.7±3.2	
	Rh-Mo	4.8±0.3	2.73±0.01	7.1±0.1	7.8±0.9	
	Rh-Fe/Mn	2.4±0.5	2.60±0.06	7.1±0.1	0.9±4.5	
0 V	Rh-O	0.1±0.1	1.88±0.05	5.2±0.1	-1.1±0.1	0.002
	Rh-Rh/Pd	2.2±0.3	2.55±0.05	7.4±0.1	-5.6±2.2	
	Rh-Mo	4.7±0.5	2.74±0.02	7.1±0.1	6.6±0.3	
	Rh-Fe/Mn	2.3±0.4	2.60±0.04	7.7±0.1	0.4±2.9	
-0.025 V	Rh-O	0.1±0.1	1.88±0.03	5.2±0.1	0.2±0.1	0.001
	Rh-Rh/Pd	2.1±0.5	2.56±0.02	7.2±0.1	-2.3±2.2	
	Rh-Mo	4.7±0.5	2.74±0.03	7.1±0.1	3.6±0.9	
	Rh-Fe/Mn	2.3±0.4	2.60±0.01	7.2±0.1	-2.0±1.6	
-0.05 V	Rh-O	0.1±0.1	1.88±0.01	5.2±0.1	0.8±0.0	0.004
	Rh-Rh/Pd	2.1±0.4	2.54±0.03	7.8±0.1	-6.7±2.9	
	Rh-Mo	4.8±0.4	2.74±0.02	7.1±0.1	3.9±4.3	
	Rh-Fe/Mn	2.3±0.2	2.60±0.01	7.1±0.1	1.5±0.5	
-0.1 V	Rh-O	0.1±0.1	1.88±0.04	5.1±0.1	1.0±1.1	0.005
	Rh-Rh/Pd	2.0±0.3	2.54±0.01	7.1±0.1	-5.8±4.5	
	Rh-Mo	4.9±0.3	2.74±0.01	7.1±0.1	5.8±2.2	
	Rh-Fe/Mn	2.2±0.3	2.60±0.01	7.1±0.1	-0.2±5.7	

REVIEWER COMMENTS

Reviewer #3 (Remarks to the Author):

The authors have addressed my comments and I would suggest to accept this nice work for publication after addressing this last point.

The authors are strongly advised to address my last question better. For the EXAFS fits you have used 16 independent parameters (Tables S11-S16). The Nyquist criterion though gives you only 10 independent parameters (considering a k-range from 3 to 11 and an R range from 1-3). This is bad scientific practise. Please redo these fits, minimizing the number of parameters to below 10, your data does not give you more. Also, having four E0 parameters does not make sense. Ideally you extract all of your scattering paths from the same structure and have as a result of it only one fitting parameter for E0.

Response to Decision Letter

September 10, 2024

Journal: Nature Communications

Reference number: NCOMMS-23-58688C

Title: Operando Visualization of Multi-Site Synergistic H₂-Production Mechanisms on Sub-Nanometric High-Entropy Metallocenes

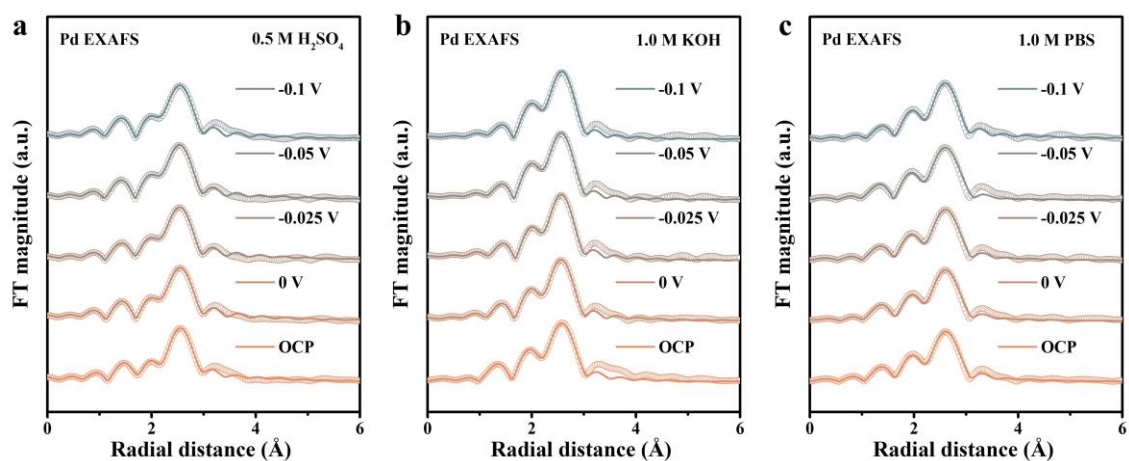
Reviewer #3 (Remarks to the Author):

The authors have addressed my comments and I would suggest to accept this nice work for publication after addressing this last point.

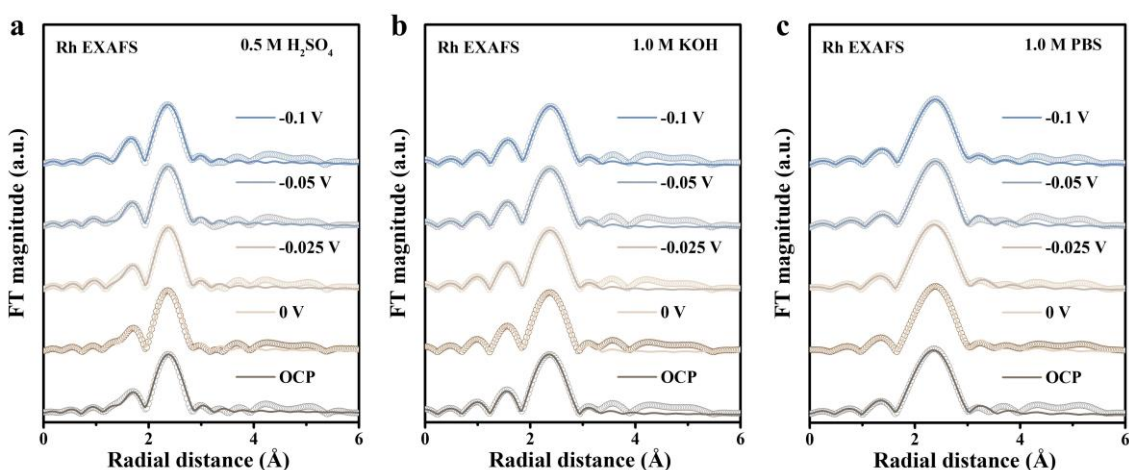
Response: We thank the reviewer for the positive comments and recommendation on the publication of this work. We also thanks for your previous constructive comments, which helped a lot for the improvement of this work. Based on this last comment, we further revised our manuscript carefully. All changes have been highlighted in the revised manuscript by formatting the text in Yellow color. Detailed lists of revisions are listed below:

Q1. The authors are strongly advised to address my last question better. For the EXAFS fits you have used 16 independent parameters (Tables S11-S16). The Nyquist criterion though gives you only 10 independent parameters (considering a k-range from 3 to 11 and an R range from 1-3). This is bad scientific practice. Please redo these fits, minimizing the number of parameters to below 10, your data does not give you more. Also, having four E0 parameters does not make sense. Ideally you extract all of your scattering paths from the same structure and have as a result of it only one fitting parameter for E0.

Response: We greatly appreciate the reviewers' comments. Considering that the atomic number of Mo (42) is close to those of Pd (44) and Rh (45), we grouped elements with similar atomic numbers, such as Mo (42), Pd (44), and Rh (45), as well as Fe (26) and Mn (25), into two separate paths. We have re-fitted the data. The fitting of the EXAFS data was conducted on the k^3 -weighted EXAFS function $\chi(k)$ within the R-range of 1-3 Å and the k-space range of 3-11 Å⁻¹. With three paths and a shared $\Delta E0$ parameter, we have minimized the parameters to below 10 to satisfy the Nyquist criterion. We have accordingly updated Supplementary Tables 10-15 and Supplementary Figures 56 and 57, and the fitting details have been updated in the SI at Line 462 and 465-467.



Supplementary Fig. 56 Operando Pd EXAFS spectra of (a) 0.5 M H₂SO₄, (b) 1.0 M KOH and (c) 1.0 M PBS without phase correction. The detailed fitting results are listed in Supplementary Tables 10, 12, and 14.



Supplementary Fig. 57 Operando Rh EXAFS spectra of (a) 0.5 M H₂SO₄, (b) 1.0 M KOH and (c) 1.0 M PBS without phase correction. The detailed fitting results are listed in Supplementary Tables 11, 13, and 15.

Supplementary Table 10. Model-fitted operando EXAFS spectra results for Pd in 0.5 M H₂SO₄.

Sample	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{\AA}^2)$	ΔE_0 (eV)	R-factor
OCP	Pd-O	0.2±0.1	2.12±0.03	4.0±0.1	1.3±5.4	0.013
	Pd-Pd/Rh/Mo	5.1±0.7	2.73±0.01	8.6±0.1		
	Pd-Fe/Mn	1.2±0.2	2.73±0.04	7.2±0.1		
0 V	Pd-O	0.2±0.1	2.12±0.01	4.1±0.1	1.3±2.4	0.007
	Pd-Pd/Rh/Mo	5.0±0.6	2.69±0.03	8.1±0.1		
	Pd-Fe/Mn	1.0±0.1	2.71±0.05	7.4±0.1		
-0.025 V	Pd-O	0.2±0.1	2.12±0.01	4.0±0.1	1.3±0.4	0.008
	Pd-Pd/Rh/Mo	4.9±0.8	2.69±0.05	8.9±0.1		
	Pd-Fe/Mn	1.1±0.1	2.72±0.03	7.1±0.1		
-0.05 V	Pd-O	0.2±0.1	2.12±0.01	3.9±0.1	1.3±5.4	0.006
	Pd-Pd/Rh/Mo	5.0±1.0	2.68±0.03	8.2±0.1		
	Pd-Fe/Mn	1.1±0.1	2.71±0.03	7.9±0.1		
-0.1 V	Pd-O	0.2±0.1	2.12±0.01	4.2±0.1	1.3±3.6	0.009
	Pd-Pd/Rh/Mo	5.1±0.9	2.69±0.03	8.1±0.1		
	Pd-Fe/Mn	1.1±0.1	2.71±0.02	7.2±0.1		

Supplementary Table 11. Model-fitted operando EXAFS spectra results for Rh in 0.5 M H₂SO₄.

Sample	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{\AA}^2)$	ΔE_0 (eV)	R-factor
OCP	Rh-O	0.3±0.2	1.88±0.01	6.2±0.1	4.4±0.3	0.005
	Rh-Rh/Pd/Mo	6.8±1.1	2.69±0.02	8.8±0.1		
	Rh-Fe/Mn	2.2±0.3	2.71±0.04	7.7±0.1		
0 V	Rh-O	0.3±0.2	1.88±0.01	5.7±0.1	4.4±1.1	0.007
	Rh-Rh/Pd/Mo	6.9±0.7	2.69±0.01	8.2±0.1		
	Rh-Fe/Mn	2.0±0.4	2.68±0.03	7.4±0.1		
-0.025 V	Rh-O	0.3±0.1	1.88±0.01	6.1±0.1	4.4±1.1	0.007
	Rh-Rh/Pd/Mo	7.0±1.0	2.70±0.02	8.4±0.1		
	Rh-Fe/Mn	2.1±0.2	2.69±0.03	7.6±0.1		
-0.05 V	Rh-O	0.3±0.2	1.88±0.01	6.2±0.1	4.4±1.1	0.007
	Rh-Rh/Pd/Mo	6.8±1.0	2.70±0.02	8.3±0.1		
	Rh-Fe/Mn	2.2±0.3	2.69±0.03	7.5±0.1		
-0.1 V	Rh-O	0.3±0.1	1.88±0.01	6.3±0.1	4.4±1.3	0.008
	Rh-Rh/Pd/Mo	7.1±0.7	2.69±0.02	8.1±0.1		
	Rh-Fe/Mn	2.3±0.2	2.72±0.03	7.3±0.1		

Supplementary Table 12. Model-fitted operando EXAFS spectra results for Pd in 1.0 M KOH.

Sample	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{Å}^2)$	ΔE_0 (eV)	R-factor
OCP	Pd-O	0.2±0.1	2.12±0.01	4.0±0.1	-0.1±2.0	0.009
	Pd-Pd/Rh/Mo	5.1±0.4	2.72±0.03	8.0±0.1		
	Pd-Fe/Mn	1.0±0.1	2.67±0.01	7.1±0.1		
0 V	Pd-O	0.4±0.1	2.12±0.02	3.6±0.1	-0.1±0.2	0.012
	Pd-Pd/Rh/Mo	5.0±0.8	2.66±0.02	7.6±0.1		
	Pd-Fe/Mn	1.1±0.1	2.64±0.04	7.0±0.1		
-0.025 V	Pd-O	0.5±0.1	2.12±0.03	4.2±0.1	-0.1±2.6	0.011
	Pd-Pd/Rh/Mo	5.1±0.9	2.70±0.02	7.9±0.1		
	Pd-Fe/Mn	1.2±0.1	2.72±0.04	7.1±0.1		
-0.05 V	Pd-O	0.6±0.1	2.12±0.02	5.1±0.1	-0.1±0.4	0.010
	Pd-Pd/Rh/Mo	5.1±0.7	2.71±0.03	8.3±0.1		
	Pd-Fe/Mn	1.4±0.1	2.73±0.04	7.1±0.1		
-0.1 V	Pd-O	0.7±0.1	2.12±0.01	6.1±0.1	-0.2±2.0	0.008
	Pd-Pd/Rh/Mo	5.0±0.5	2.69±0.05	8.6±0.1		
	Pd-Fe/Mn	1.5±0.1	2.70±0.04	7.5±0.1		

Supplementary Table 13. Model-fitted operando EXAFS spectra results for Rh in 1.0 M KOH.

Sample	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{\AA}^2)$	ΔE_0 (eV)	R-factor
OCP	Rh-O	0.2±0.1	1.88±0.01	6.2±0.1	0.8±0.8	0.008
	Rh-Rh/Pd/Mo	6.8±0.9	2.70±0.04	8.4±0.1		
	Rh-Fe/Mn	2.3±0.1	2.73±0.02	7.6±0.1		
0 V	Rh-O	0.2±0.1	1.88±0.01	6.2±0.1	0.9±2.7	0.007
	Rh-Rh/Pd/Mo	6.9±0.9	2.69±0.03	8.1±0.1		
	Rh-Fe/Mn	2.4±0.3	2.74±0.05	7.3±0.1		
-0.025 V	Rh-O	0.3±0.1	1.88±0.01	6.2±0.1	0.8±3.1	0.011
	Rh-Rh/Pd/Mo	6.9±0.7	2.71±0.02	8.3±0.1		
	Rh-Fe/Mn	2.2±0.1	2.70±0.06	7.3±0.1		
-0.05 V	Rh-O	0.3±0.1	1.88±0.01	6.2±0.1	0.8±2.2	0.008
	Rh-Rh/Pd/Mo	7.1±1.1	2.69±0.03	8.1±0.1		
	Rh-Fe/Mn	2.1±0.1	2.71±0.03	7.1±0.1		
-0.1 V	Rh-O	0.3±0.2	1.88±0.02	6.2±0.1	0.8±1.9	0.008
	Rh-Rh/Pd/Mo	6.9±0.3	2.72±0.03	8.4±0.1		
	Rh-Fe/Mn	2.4±0.1	2.70±0.05	7.3±0.1		

Supplementary Table 14. Model-fitted operando EXAFS spectra results for Pd in 1.0 M PBS.

Sample	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{\AA}^2)$	ΔE_0 (eV)	R-factor
OCP	Pd-O	0.2±0.1	2.12±0.02	4.0±0.1	-2.0±1.1	0.012
	Pd-Pd/Rh/Mo	5.2±0.9	2.73±0.03	8.5±0.1		
	Pd-Fe/Mn	0.9±0.1	2.67±0.03	7.6±0.1		
0 V	Pd-O	0.2±0.1	2.12±0.08	4.1±0.1	-2.2±1.0	0.009
	Pd-Pd/Rh/Mo	5.3±0.7	2.69±0.02	8.6±0.1		
	Pd-Fe/Mn	1.1±0.2	2.71±0.06	7.5±0.1		
-0.025 V	Pd-O	0.2±0.1	2.12±0.01	4.1±0.1	-2.2±1.0	0.011
	Pd-Pd/Rh/Mo	5.2±1.0	2.71±0.03	8.3±0.1		
	Pd-Fe/Mn	1.2±0.1	2.72±0.05	7.8±0.1		
-0.05 V	Pd-O	0.2±0.1	2.12±0.02	4.1±0.1	-2.0±3.7	0.009
	Pd-Pd/Rh/Mo	5.2±0.9	2.70±0.03	8.5±0.1		
	Pd-Fe/Mn	1.4±0.2	2.71±0.05	7.2±0.1		
-0.1 V	Pd-O	0.3±0.1	2.12±0.02	4.1±0.1	-2.0±1.0	0.007
	Pd-Pd/Rh/Mo	5.3±0.7	2.71±0.02	8.3±0.1		
	Pd-Fe/Mn	1.4±0.2	2.69±0.05	7.7±0.1		

Supplementary Table 15. Model-fitted operando EXAFS spectra results for Rh in 1.0 M PBS.

Sample	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{\AA}^2)$	ΔE_0 (eV)	R-factor
OCP	Rh-O	0.2±0.1	1.88±0.05	5.3±0.1	1.1±0.2	0.013
	Rh-Rh/Pd/Mo	7.1±1.2	2.66±0.02	7.6±0.1		
	Rh-Fe/Mn	1.8±0.5	2.64±0.08	8.1±0.1		
0 V	Rh-O	0.1±0.1	1.88±0.05	5.2±0.1	1.1±0.1	0.010
	Rh-Rh/Pd/Mo	6.9±1.1	2.65±0.01	7.4±0.1		
	Rh-Fe/Mn	1.8±0.4	2.62±0.04	8.1±0.1		
-0.025 V	Rh-O	0.1±0.1	1.88±0.03	5.2±0.1	1.0±0.4	0.009
	Rh-Rh/Pd/Mo	7.1±0.8	2.66±0.02	7.2±0.1		
	Rh-Fe/Mn	2.0±0.2	2.63±0.06	8.3±0.1		
-0.05 V	Rh-O	0.1±0.1	1.88±0.01	5.2±0.1	1.0±0.1	0.007
	Rh-Rh/Pd/Mo	7.2±1.0	2.64±0.03	7.8±0.1		
	Rh-Fe/Mn	1.9±0.2	2.61±0.07	8.4±0.1		
-0.1 V	Rh-O	0.1±0.1	1.88±0.04	5.1±0.1	1.1±0.2	0.008
	Rh-Rh/Pd/Mo	7.0±1.3	2.65±0.01	7.0±0.1		
	Rh-Fe/Mn	1.8±0.5	2.60±0.03	7.9±0.1		

Finally, we hope that all concerns have been addressed. Thank you very much again for your attention and kindness to improve our work.

REVIEWER COMMENTS

Reviewer #3 (Remarks to the Author):

The authors have now fitted their XAFS spectra just within the Nyquist conditions (10 free parameters, 10 parameters used). With that they have addressed my last comment and I can accept the manuscript.

And maybe having now these results in hand (to be addressed on the authors discretion, not required by me): From these results it is clear that not only Pd has Pd-O neighbours, but also Rh. Can you really claim that O is activated on Pd?

Response to Decision Letter

September 16, 2024

Journal: Nature Communications

Reference number: NCOMMS-23-58688D

Title: Operando Visualization of Multi-Site Synergistic H₂-Production Mechanisms on Sub-Nanometric High-Entropy Metallenes

Reviewer #3 (Remarks to the Author):

The authors have now fitted their XAFS spectra just within the Nyquist conditions (10 free parameters, 10 parameters used). With that they have addressed my last comment and I can accept the manuscript.

Response: We thank the reviewer for the positive comments and recommendation on the publication of this work, also thanks for your previous constructive comments, which helped a lot for the improvement of this work. For this additional comment, the detailed discussion and responses are as follows:

And maybe having now these results in hand (to be addressed on the authors discretion, not required by me): From these results it is clear that not only Pd has Pd-O neighbours, but also Rh. Can you really claim that O is activated on Pd?

Response: We greatly appreciate the reviewer's comments. First, when the prepared HEMs are exposed to air, a small amount of under-coordinated corner atoms and edge atoms with stronger oxyphilic nature on the catalyst surface can be oxidized. Therefore, both Pd and Rh elements in the prepared HEMs samples have a small amount of Pd-O and Rh-O neighbours. This phenomenon is very common in the reported literature [Nature 574, 81-85 (2019); ACS Nano 16, 522-532 (2022)]. Even on the surface of Pd foil, there will be a small amount of oxidized Pd atoms. According to previous reports, the HER activity of metal oxides is usually very poor. Its contribution to the activity of the overall material is very small. We also tested the HER performance of PdO and RhO₂. As shown in Supplementary Fig. 7, the HER activity of PdRhMoFeMn HEMs is far superior to PdO and RhO₂. In the reported literature, researchers usually focus on the main material and ignore the small amount of surface metal oxide species that have little impact on the research results [Nat. Commun. 13, 2662 (2022); Nat. Commun. 15, 359 (2024); Adv. Mater. 36, 2309715 (2023)]. The relevant discussion is in Lines 196-203 of the main manuscript. In addition, Fig. 7c and

Supplementary Table 12 show a slight increase in both the Pd-O peak intensity and coordination numbers during the catalytic reaction, indicating the presence of some chemisorbed oxygen on Pd sites (Lines 463-467). This result, when discussed alongside the theoretical calculations and Tafel slope analysis, indicates a possible water dissociation process occurring at Pd sites (Lines 482-484). Under acidic conditions, the Pd-O peak intensity does not change significantly because acidic HER does not require the step of water dissociation to produce protons. However, relative to the initial Rh-O peak intensity and coordination numbers, there is no obvious change in these values with increasing potential under both acidic and alkaline conditions, indicating the negligible adsorption of chemisorbed oxygen species on the Rh sites (Fig. 7b,d and Supplementary Tables 11 and 13).

Finally, we hope that all concerns have been addressed. Thank you very much again for your attention and kindness to improve our work.