

Heteroatom dopants overcome the activity-stability trade-off in RuO₂ for acidic oxygen evolution

Corresponding Author: Professor Yongwen Tan

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

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This manuscript reports a Ta and B co-doped nanoporous RuO₂ electrocatalyst that employs heteroatom doping to address the activity-stability trade-off in acidic OER. The Ru-O-Ta framework stabilizes Ru sites by mediating oxygen bonds and replenishing vacancies, while Ru-O-Ta/B active sites lower energy barriers and improve catalytic performance by optimizing charge distribution. This study presents a robust and systematic strategy to significantly enhance the performance of Ru-based catalysts for the acidic OER in PEMWE. Upon addressing the following issues, I recommend this work for publication in Nature Communications.

1. The author performed a series of in-situ characterizations to elucidate the structure-activity relationship and OER mechanism of the catalyst. There is no specific explanation provided for the decrease in the Ru-M peak in the in situ XAS section (Figure 3c).
2. Does the internal alloy structure affect the activity of the external oxide layer?
3. The author analyzed the oxidation state changes during the in-situ XAS process using absorption edge shifts and white line peak rises. However, the rationale and distinctions behind these different analysis methods should be further explained.
4. To enhance the clarity of the preparation process, it is suggested that the author provide additional characterizations regarding the nanoporous Ta-RuB₂.
5. The author is recommended to carefully check the double-layer capacitance testing section (Supplementary Figure 14), as there appears to be a slight labeling error.

Reviewer #2

(Remarks to the Author)

The authors described the preparation and characterization of Ta-/B-RuO₂ catalysts for OER. Despite a lot of methods and techniques applied, the data analysis and conclusions made based on the obtained results have to be further revisited. The manuscript should be revised by checking the following points (that will in the affect their final conclusions):

1. Fig. 11 and 15 in SI : Ru3p spectra analysis, why Ru³⁺ peak is located higher than Ru⁴⁺ ? Figure 11a, Ru3p peak in B-RuO₂ sample has a shoulder at the position of Ta 4p_{1/2} (while it is Ta-free sample), however it was not identified in the spectra ? Is it Ta contamination ? Please comment on this shoulder and provide its analysis.
2. O1s XPS : the authors claim that the peak at 532.3 eV is related to oxygen vacancies. How it was proven ? One typically observes -OH groups at this position. Please comment on the assignment.
3. The authors claim that the oxidation state of Ru based on XAS data is between 0 and +4, while based on the Ru K edge spectra, it seems like Ru state is close to RuO₄, where small difference in the rising edge can be related to the Ta/B bonding. Just an elongation of Ru-O bonds may lead to the changes in Ru K edge spectra. Please, comment on this.
4. Fig. 1g is not clear, there is a red spectra of Ta/B-RuO₂ sample, and then Ta foil and KTaO₃ spectra position are indicated. However, the positions of the both references overlap, so why authors claim that there is Ta⁺⁵ in Ta/B-RuO₂ ? Or the marks in Fig. 1g correspond to the spectra intensity ? In this why there is no shift in the white line for Ta foil and KTaO₃, the local coordination is not the same for a metal and KTaO₃, one would assume different line shapes as well. Please

provide the reference spectra and discuss this part more in detail.

5. What about Ru exafs ? do you have these data ? It would be nice to compare RuO₂ and Ta/B-RuO₂

6. The authors compared the OER performance for the synthesized catalyst and commercial RuO₂. However, no information on the commercial catalyst is given. Where it is coming from, its structure, particles size (XPS, XAS, TEM etc). This is important for further comparison. If the commercial particles are >100nm it is not fair to compare with a synthesized catalyst with few nms particles size.

7. Tafel slope for RuO₂ of 96 mV dec⁻¹ seems high. How does this value correspond to the literature values ? for example, in "Mechanism and Tafel Lines of Electro-Oxidation of Water to Oxygen on RuO₂(110)" (J. Am. Chem. Soc. 2010, 132, 51, 18214–18222): "The kinetics model based on this mechanism has been utilized to rationalize the measured current~overpotential (log(j)~η) plot, known as the Tafel line, which was commonly utilized for the assessment of the electrode performance for OER. There are two clear Tafel lines observed for OER on RuO₂, one at the lower potentials (e.g., < ~1.52 V) with a slope of 30–60 mV (i.e., 59 mV on RuO₂(110); 30–60 mV on RuO₂ particles) and another at the higher potentials with a slope of ~120 mV. (13, 14)" Discuss this point, as well as 2 different Tafel slopes observed in the literature.

8. Operando XAS. Shift of Ru edge does not mea100% an increase in oxidation state, but rather some small changes in bond distances, that may further lead to the change in the oxidation state. The observed changes in Ru and Ta edges are tiny, the spectra should change their shape no ? Can it be related to the small surface contribution to the overall data ? Would be interesting to compare these results with similar operando XAS on a commercial RuO₂.

9. The FT-EXAFS data can be improved. Specifically, the intensity at 1 Å and below do not have any physical meaning, so the intensity should be at 0 there. The authors need to proper discuss the changes they see. If Ru-M does not change, why Ta-M is changing ?

10. Raman spectra does not seem to be identical, despite the authors' phrase : "In contrast, the consistent Raman signal observed for Ta/B-RuO₂ 199 indicated that its crystal structure remains remarkably stable under OER conditions". Please, revise this part.

11. DEMS results presented in Figure 4 are missing the error bars.

Reviewer #3

(Remarks to the Author)

For the theoretical section, the authors performed standard first-principles calculations to investigate the OER performance of boron-tantalum co-doped RuO₂. However, the computational methodology lacks rigor, and the following suggestions are provided for improvement:

1. Lack of references in the computational details. Please cite relevant literature to validate the methodology.

2. As shown in Figure S18, the slab model appears to lack fixed atomic layers, which may lead to unrealistic surface relaxation during optimization. To ensure stability, it is standard practice to immobilize the bottom 2–3 layers. Please revise the model accordingly.

3. In Figure 5a, what is the isosurface value of electron gas in charge density difference? What did the color represent?

4. How were the B/Ta doping sites determined? A systematic comparison of different sites and their formation energies are needed

5. In Figure 5c and 5d, how about the hybridization between O/B p-orbital and Ru d-orbital?

6. In Figure 5e, the authors mentioned the gap between Ru d-orbital and O p-orbital. Please provide more explanation. How about the B element?

7. In Figure 5g, B-doping is absent in B-RuO₂ whereas B/Ta RuO₂ shows B doping in the bottom layer. Why?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have addressed all my questions. Therefore, I suggest that it could be accepted.

Reviewer #2

(Remarks to the Author)

The manuscript has been nicely improved and can be published as it is.

Reviewer #3

(Remarks to the Author)

Please provide the VASP input files, specifically the INCAR configuration and optimized-geometry CONTCAR file, in the Supporting Information section.

The authors have addressed our comments, and no additional questions remain.

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Response to Reviewers' Comments

At first, we would like to express our sincere gratitude to all the reviewers for their valuable and thoughtful comments, which have provided us with constructive insights to significantly improve the quality of our manuscript. We have conducted more experiments and analyses to address the raised concerns. Below, we provide detailed responses to each comment, along with specific revisions made to the manuscript.

Reviewer #1:

This manuscript reports a Ta and B co-doped nanoporous RuO₂ electrocatalyst that employs heteroatom doping to address the activity-stability trade-off in acidic OER. The Ru-O-Ta framework stabilizes Ru sites by mediating oxygen bonds and replenishing vacancies, while Ru-O-Ta/B active sites lower energy barriers and improve catalytic performance by optimizing charge distribution. This study presents a robust and systematic strategy to significantly enhance the performance of Ru-based catalysts for the acidic OER in PEMWE. Upon addressing the following issues, I recommend this work for publication in Nature Communications.

Reply: We sincerely appreciate the Reviewer's valuable comments, which can enhance the quality and clarity of our work.

1. The author performed a series of in-situ characterizations to elucidate the structure-activity relationship and OER mechanism of the catalyst. There is no specific explanation provided for the decrease in the Ru-M peak in the in situ XAS section (Figure 3c).

Reply: We sincerely appreciate the reviewer for this comment. The intensity of the Ru-M shell is intricately correlated with both the coordination number and the degree of structural disorder. Given that the Ru core does not directly interact with the electrolyte and is not actively involved in the OER, the observed variations in intensity should be ascribed to the structural disorder that is induced by the oscillations occurring during the OER process. This discussion has been incorporated into the relevant section.

2. Does the internal alloy structure affect the activity of the external oxide layer?

Reply: We sincerely appreciate the reviewer's insightful suggestion. The surface oxide layer, with a thickness of approximately 5 nm (**Figure R1**), effectively suppresses the electronic coupling interactions between the internal alloy matrix and the surface-active sites. As a result, the internal alloy structure has a negligible impact on the catalytic activity of the surface oxide layer, thereby ensuring the catalytic properties of the surface layer are predominantly determined by its own characteristics (**Ref. 2**). We have added relevant descriptions in the Supplementary Information.

Ref. 2 in Supplementary Information: Jiang, K. et al. Transition-Metal Single Atoms in a Graphene Shell as Active Centers for Highly Efficient Artificial Photosynthesis. *Chem* **3**, 950-960 (2017).

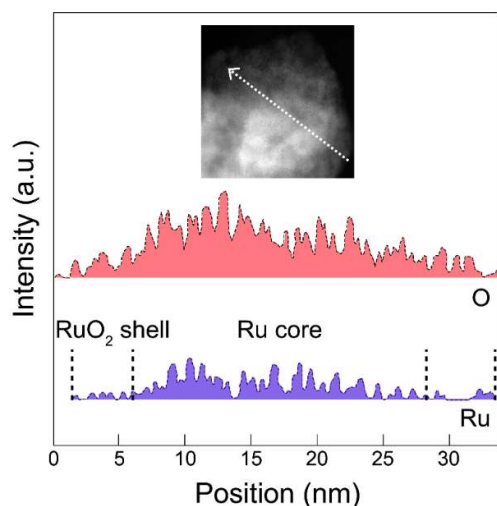


Figure R1. STEM-EDX line profile across a ligament.

3. The author analyzed the oxidation state changes during the in-situ XAS process using absorption edge shifts and white line peak rises. However, the rationale and distinctions behind these different analysis methods should be further explained.

Reply: We sincerely appreciate the reviewer's insightful comment.

For Ru K-edge analysis:

The Ru K-edge position is governed by the effective nuclear charge experienced by the $1s$ core electrons. As the oxidation state of Ru increases, the loss of valence electrons (e.g., $4d/5s$ electrons) reduces electron shielding, increasing the effective nuclear charge. This strengthens the $1s$ electron binding energy, thereby raising the energy required for $1s \rightarrow 4p$ transitions and shifting the absorption edge to higher energies.

For Ta L_3 -edge analysis:

The white line intensity at the Ta L_3 -edge arises from $2p_{3/2} \rightarrow 5d$ electronic transitions. Higher oxidation states of Ta (e.g., Ta^{5+} vs. Ta^{3+}) correlate with increased unoccupied $5d$ states due to electron depletion. This enhanced density of empty $5d$ states amplifies the transition probability, resulting in greater white line intensity.

This explains the rationale behind our different analysis methods, and we have incorporated this discussion into the manuscript.

4. To enhance the clarity of the preparation process, it is suggested that the author provide additional characterizations regarding the nanoporous Ta-RuB₂.

Reply: We sincerely thank the reviewer for the valuable suggestion. We have incorporated more characterization data to further elucidate the properties of the nanoporous Ta-RuB₂. Specifically, we have added SEM images and the corresponding SEM-EDS spectra (**Figure R2**) in the Supporting Information. These data provide detailed insights into the morphological and compositional

characteristics of the material.

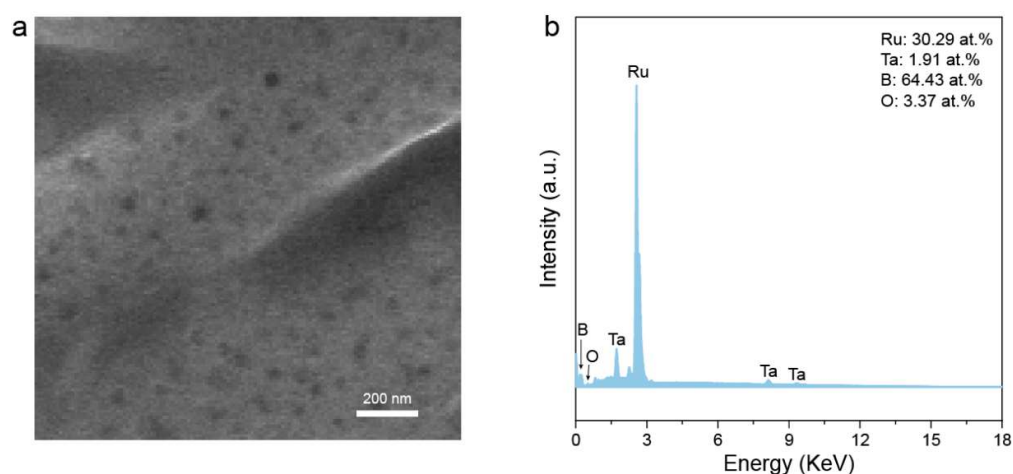


Figure R2. (a) SEM image of Ta-RuB₂. (b) SEM-EDS spectrum of Ta-RuB₂.

5. The author is recommended to carefully check the double-layer capacitance testing section (Supplementary Figure 14), as there appears to be a slight labeling error.

Reply: We sincerely thank the reviewer for their meticulous attention to this detail. We have now rectified the error, as depicted in **Figure R3**.

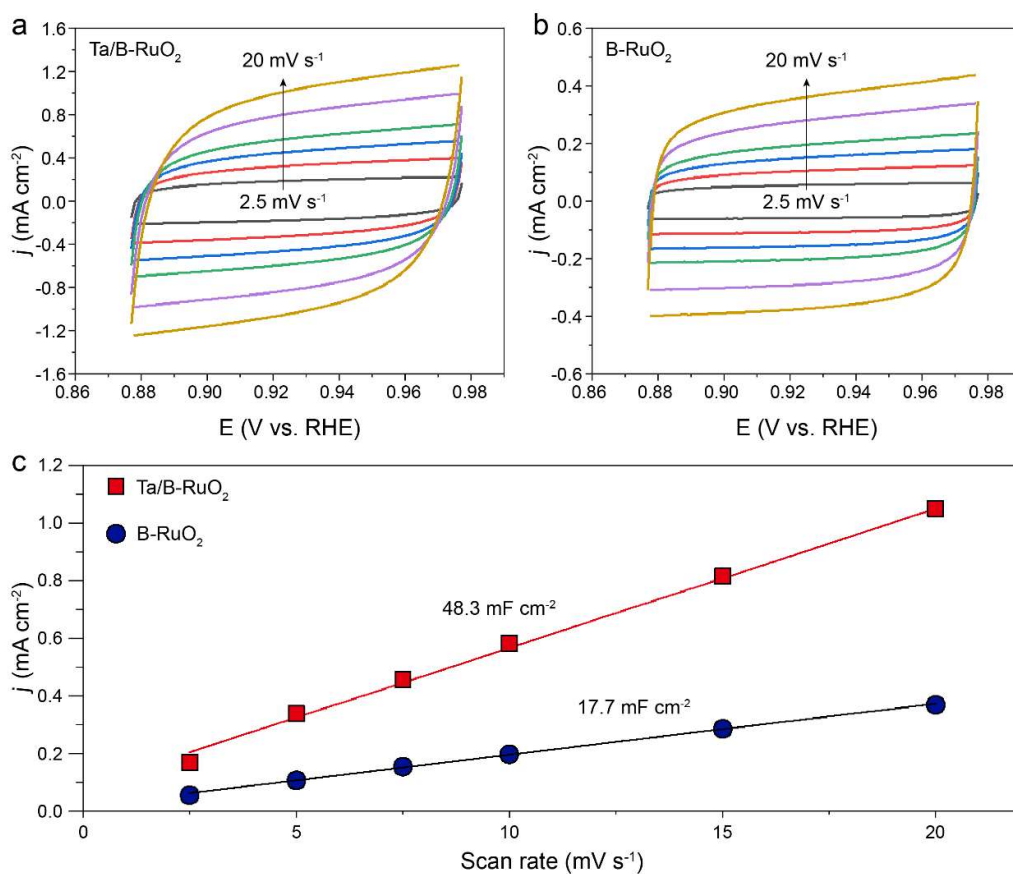


Figure R3. Typical cyclic voltammograms at the scan rates ranging from 2.5 to 20 mV s⁻¹ of (a) Ta/B-RuO₂ and (b) B-RuO₂. (c) The linear fitting of the capacitive current densities versus the scan rates.

Reviewer #2:

The authors described the preparation and characterization of Ta-/B-RuO₂ catalysts for OER. Despite a lot of methods and techniques applied, the data analysis and conclusions made based on the obtained results have to be further revisited. The manuscript should be revised by checking the following points (that will in the affect their final conclusions):

Reply: We are deeply appreciative of your comprehensive evaluation and astute observations on our manuscript. Your insightful comments have spurred us to re-evaluate key analyses and refine our discussions, particularly in the areas of data interpretation and conclusions. As a result, we have conducted a meticulous revision of the text, which has significantly enhanced the scientific rigor of our study.

1. Fig. 11 and 15 in SI: Ru 3*p* spectra analysis, why Ru³⁺ peak is located higher than Ru⁴⁺? Figure 11a, Ru 3*p* peak in B-RuO₂ sample has a shoulder at the position of Ta 4*p*_{1/2} (while it is Ta-free sample), however it was not identified in the spectra? Is it Ta contamination? Please comment on this shoulder and provide its analysis.

Reply: We sincerely appreciate your insightful questions. We have carefully reviewed the relevant literature and found that the binding energy of Ru³⁺ is typically higher than that of Ru⁴⁺ in the XPS spectra of Ru 3*p*, a phenomenon widely documented in the literature (Ref. 20, 36, 41). The reasons are as follows:

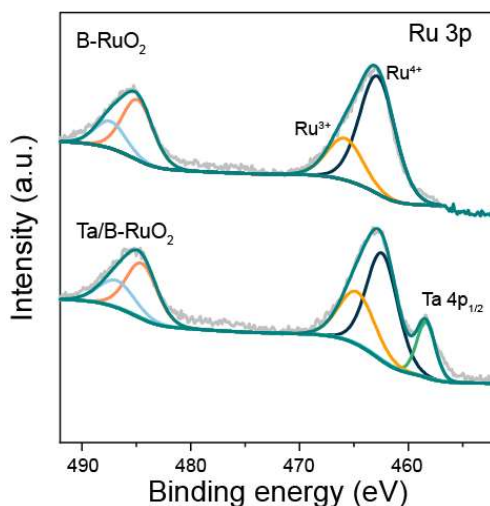


Figure R4. High-resolution Ru 3*p* XPS spectra of Ta/B-RuO₂ and B-RuO₂.

When Ru³⁺ (*d*⁵) is in a high-spin state (e.g., in an octahedral crystal field), the stronger electron-electron repulsion among its *d*-electrons may lead to an increase in binding energy (BE). Conversely, if Ru⁴⁺ (*d*⁴) adopts a low-spin state, its electrons are more tightly bound due to reduced repulsion, which could

result in a lower BE. This spin-state difference can potentially invert the expected relationship between oxidation state and BE. Regarding the shoulder peak observed in the B-RuO₂ sample, our further analysis suggests that this may arise from an inappropriate fitting approach. To address this issue, we have conducted a re-fitting of the XPS spectrum for the B-RuO₂ sample, ensuring the accuracy and scientific validity of the results. The re-fitted results are presented in **Figure R4**.

Ref. 20: Zhang, D.-F. et al. Construction of Zn-doped RuO₂ nanowires for efficient and stable water oxidation in acidic media. *Nat. Commun.* **14**, 2517 (2023).

Ref. 36: Boakye, F. O. et al. Synergistic Engineering of Dopant and Support of Ru Oxide Catalyst Enables Ultrahigh Performance for Acidic Oxygen Evolution. *Adv. Funct. Mater.* **34**, 2408714 (2024).

Ref. 41: Deng, L.-M. et al. Valence Oscillation of Ru Active Sites for Efficient and Robust Acidic Water Oxidation. *Adv. Mater.* **35**, 2305939 (2023).

2. O1s XPS: the authors claim that the peak at 532.3 eV is related to oxygen vacancies. How it was proven? One typically observes ¹⁸OH groups at this position. Please comment on the assignment.

Reply: We sincerely appreciate your insightful comments. Initially, through a thorough review of the literature, we identified the peak at this position as corresponding to oxygen vacancies (Ov), as illustrated in **Figure R5** (**Ref. 19, 42**). Upon meticulous re-examination, we detected a mislabeling of the Ov peak position in Ta/B-RuO₂; it should actually be positioned at 531.8 eV (**Supplementary Figure 13**). This peak exhibits a pronounced positive shift relative to B-RuO₂, indicating a significant alteration in their chemical environment.

[FIGURE REDACTED]

Figure R5. O 1s XPS spectra of Rh-RuO₂/G and RuO₂/G (**Ref. 19**).

Ref. 19: Wang, Y. et al. Unraveling oxygen vacancy site mechanism of Rh-doped RuO₂ catalyst for long-lasting acidic water oxidation. *Nat. Commun.* **14**, 1412 (2023).

Ref. 42: Oh, D. et al. Unassisted electrochemical H₂O₂ production coupled to glycerol oxidation. *Nat. Synth.* DOI: 10.1038/s44160-025-00774-y.

3. The authors claim that the oxidation state of Ru based on XAS data is between 0 and +4, while based on the Ru K-edge spectra, it seems like Ru state is close to RuO₄, where small difference in the rising edge can be related to the Ta/B bonding. Just an elongation of Ru-O bonds may lead to the changes in Ru-K edge spectra. Please comment on this.

Reply: We sincerely appreciate your insightful and comprehensive comments. In this study, we employed ex-situ spectroscopy to confirm the oxidation state of Ru in Ta/B-RuO₂. As illustrated in

Figure R6a, the absorption edge of Ru in Ta/B-RuO₂ is positioned between that of Ru foil (representing the 0-oxidation state) and RuO₂ (representing the +4-oxidation state), indicating that the oxidation state of Ru in Ta/B-RuO₂ lies between 0 and +4 (**Ref. 29, 41**).

Besides, XANES involves photoelectron excitation and multiple scattering, reflecting medium-range order like coordination symmetry and electronic states. EXAFS is based on single scattering by neighboring atoms, revealing short-range order such as bond lengths, coordination numbers, and atomic species. XANES is commonly used to determine the oxidation states of elements. In contrast, EXAFS is employed to measure bond lengths and coordination numbers, as well as to distinguish between different neighboring atomic species. Therefore, the offset of the absorption edge is more sensitive to changes in the oxidation state, while the elongation of Ru-O bonds should be attributed to the doping of heteroatoms.

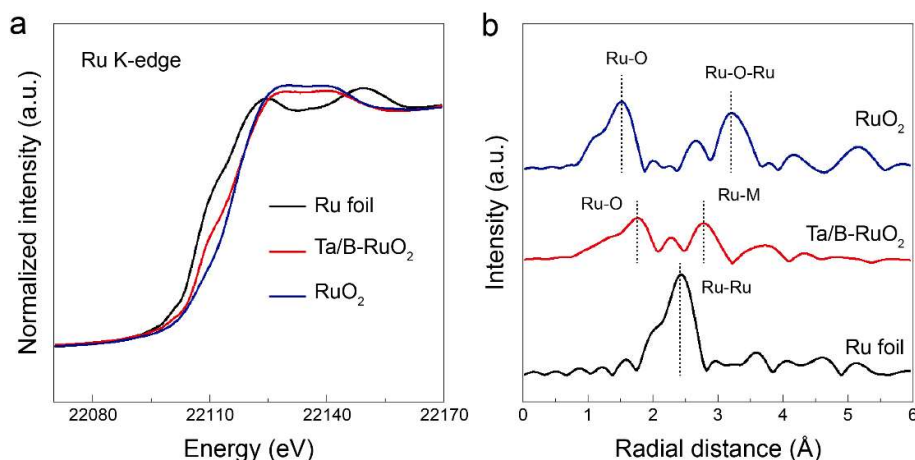


Figure R6. (a) Ru K-edge XANES spectra of Ta/B-RuO₂. (b) The corresponding Ru K-edge FT-EXAFS spectra.

Ref. 29: Liu, Y. et al. Ultrathin and Conformal Depletion Layer of Core/Shell Heterojunction Enables Efficient and Stable Acidic Water Oxidation. *J. Am. Chem. Soc.* **146**, 26897-26908 (2024).

Ref. 41: Deng, L.-M. et al. Valence Oscillation of Ru Active Sites for Efficient and Robust Acidic Water Oxidation. *Adv. Mater.* **35**, 2305939 (2023).

4. Fig. 1g is not clear, there is a red spectrum of Ta/B-RuO₂ sample, and then Ta foil and KTaO₃ spectra position are indicated. However, the positions of the both references overlap, so why authors claim that there is Ta⁺⁵ in Ta/B-RuO₂? Or the marks in Fig. 1g correspond to the spectra intensity? In this why there is no shift in the white line for Ta foil and KTaO₃, the local coordination is not the same for a metal and KTaO₃, one would assume different line shapes as well. Please provide the reference spectra and discuss this part more in detail.

Reply: We sincerely appreciate the insightful question raised by the reviewer. In this study, the oxidation state of Ta in Ta/B-RuO₂ was determined by comparing the intensity of the white line peaks. For this purpose, we referenced the white line intensities of Ta foil (representing the 0-oxidation state) and KTaO₃ (representing the +5-oxidation state) from the literature (**Ref. 43**). To facilitate a more

intuitive comparison between Ta/B-RuO₂, KTaO₃, and Ta foil, we have included their corresponding spectra in **Figure R7**. The white line intensity of Ta in Ta/B-RuO₂ was found to be close to that of KTaO₃, which confirms that the valence state of Ta is close to +5.

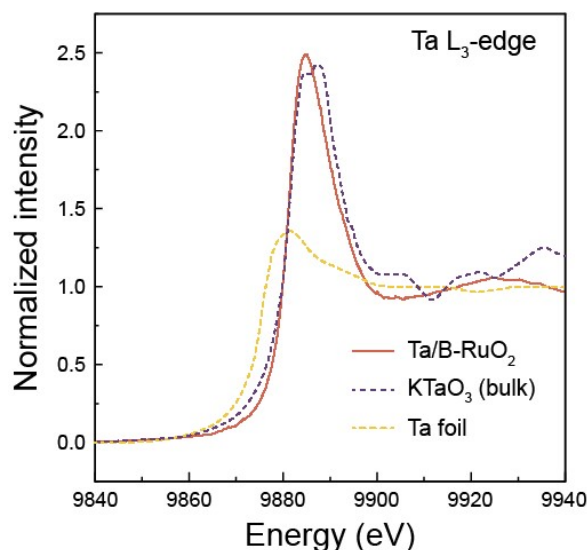


Figure R7. Ta L₃-edge XANES of Ta/B-RuO₂, KTaO₃ (bulk) and Ta foil.

Ref. 43: Liu, C.-J. et al. Two-dimensional superconductivity and anisotropic transport at KTaO₃ (111) interfaces. *Science* **371**, 716-721 (2021).

5. What about Ru EXAFS? do you have these data? It would be nice to compare RuO₂ and Ta/B-RuO₂.

Reply: We express our sincere appreciation for the reviewer's insightful suggestion. We have provided Ru EXAFS data for both RuO₂ and Ta/B-RuO₂ to facilitate a comparative analysis (**Figure R6**).

6. The authors compared the OER performance for the synthesized catalyst and commercial RuO₂. However, no information on the commercial catalyst is given. Where it is coming from, its structure, particles size (XPS, XAS, TEM etc.). This is important for further comparison. If the commercial particles are >100 nm it is not fair to compare with a synthesized catalyst with few nms. particles size.

Reply: We sincerely appreciate the reviewer's suggestions.

Following your suggestion, we have provided further information (**Methods** in manuscript) and characterization of RuO₂, including XAS (**Figure R6**), EPR (**Figure 1h** in manuscript), SEM (**Figure R8**), and XPS (**Figure R9**).

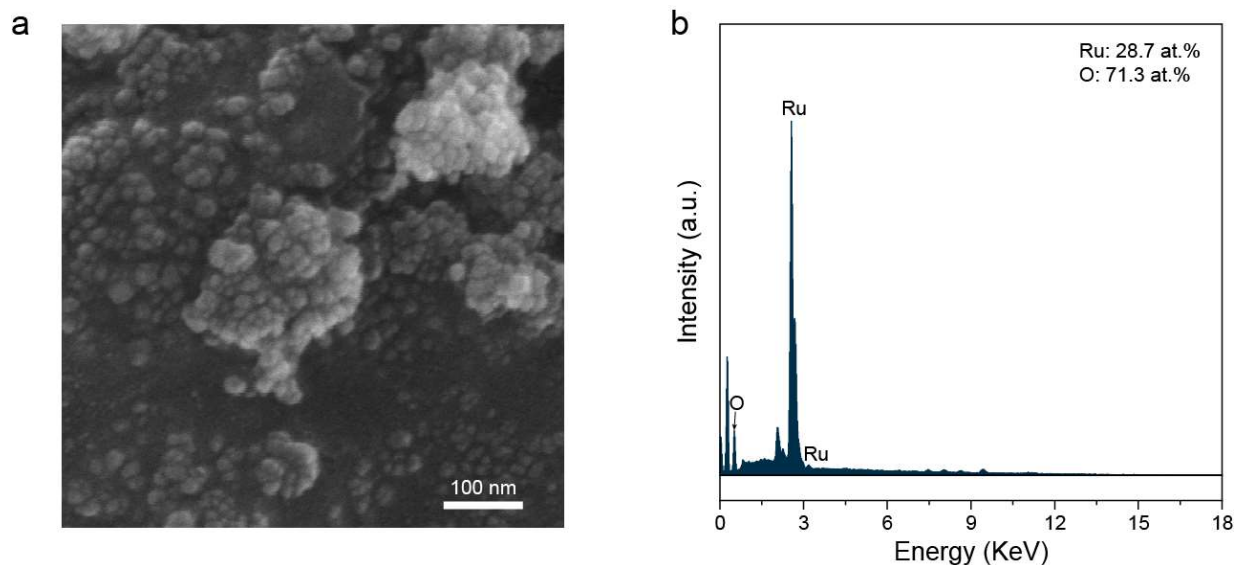


Figure R8. (a) SEM image of RuO₂. (b) SEM-EDS spectrum of RuO₂.

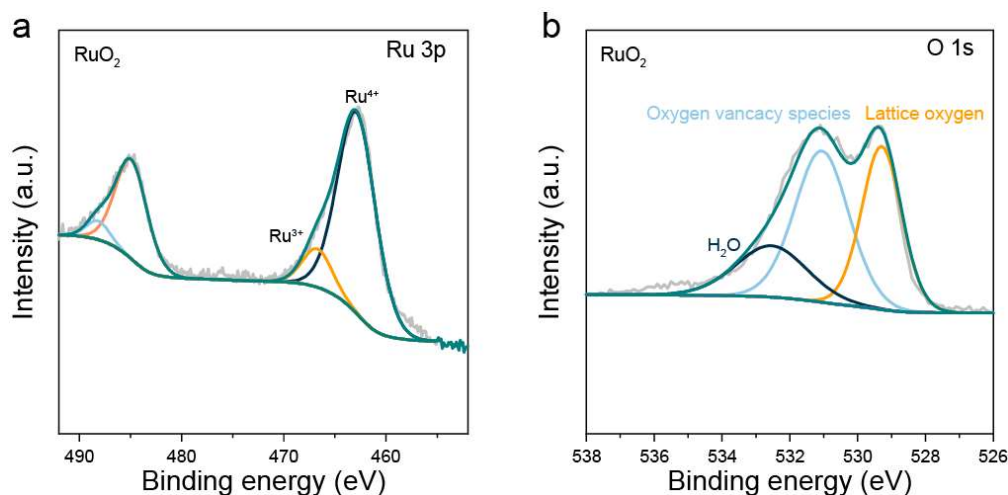


Figure R9. High-resolution XPS spectra of RuO₂ at (a) Ru 3p and (b) O 1s.

Based on the SEM analysis, the morphology of RuO₂ is characterized as an agglomerate comprising spherical particles with a diameter of approximately 20 nm. Despite the disparities in morphology and scale, comparing synthesized catalysts with commercial RuO₂ remains scientifically valid. The incorporation of heteroatom dopants and the nanoscale structure of the synthesized catalysts significantly enhance their activity and stability.

7. Tafel slope for RuO₂ of 96 mV dec⁻¹ seems high. How does this value correspond to the literature values? For example, in “Mechanism and Tafel Lines of Electro-Oxidation of Water to Oxygen on RuO₂(110)” (J. Am. Chem. Soc. 2010, 132, 51, 18214-18222): “The kinetics model based on this mechanism has been utilized to rationalize the measured current~overpotential (log(*j*)~ η) plot, known as the Tafel line, which was commonly utilized for the assessment of the electrode performance for

OER. There are two clear Tafel lines observed for OER on RuO₂, one at the lower potentials (e.g., < ~1.52 V) with a slope of 30-60 mV (i.e., 59 mV on RuO₂(110); 30-60 mV on RuO₂ particles) and another at the higher potentials with a slope of ~120 mV. (13, 14)” Discuss this point, as well as 2 different Tafel slopes observed in the literature.

Reply: We sincerely appreciate the reviewer for raising this insightful suggestion. We have conducted a reanalysis of the Tafel slopes of RuO₂ across various potentials. As depicted in **Figure R10**, the Tafel slope is found to be 69 mV dec⁻¹ at low potentials, which increases to 138 mV dec⁻¹ at high potentials. These findings are generally consistent with the literature cited by the reviewer, although minor discrepancies may arise from differences in experimental conditions. In addition, we cited the following literature as references:

Ref. 44: Fang, Y.-H. & Liu, Z.-P. Mechanism and Tafel Lines of Electro-Oxidation of Water to Oxygen on RuO₂(110). *J. Am. Chem. Soc.* **132**, 18214-18222 (2010).

Ref. 54: Guerrini, E., Trasatti, S. Recent developments in understanding factors of electrocatalysis. *Russ. J. Electrochem.* **42**, 1017 (2006).

Ref. 55: Castelli, P. et al. Single crystals as model electrocatalysts: Oxygen evolution on RuO₂ (110). *J. Electroanal. Chem.* **210**, 189 (1986).

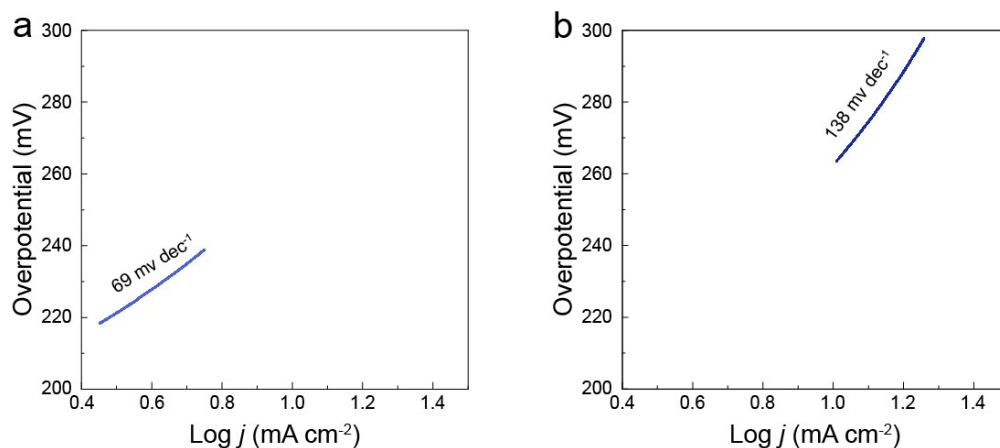


Figure R10. Tafel plots of RuO₂ at (a) low potential and (b) high potential.

8. Operando XAS. Shift of Ru edge does not mean 100% an increase in oxidation state, but rather some small changes in bond distances, that may further lead to the change in the oxidation state. The observed changes in Ru and Ta edges are tiny, the spectra should change their shape, no? Can it be related to the small surface contribution to the overall data? Would be interesting to compare these results with similar operando XAS on a commercial RuO₂.

Reply: We sincerely appreciate the reviewer for their insightful comments. We agree with the reviewer's opinion that the shift of the absorption edge may be associated with changes in bond length. However, in our study, we observed that alterations in bond length did not correspond to shifts in the absorption edge (**Figure R11**). Additionally, considering the unique characteristics of the OER, we posit that shifts in the absorption edge may be more sensitive to changes in oxidation states. The

following reason accounts for this observation:

The Ru K-edge position is governed by the effective nuclear charge experienced by the 1s core electrons. As the oxidation state of Ru increases, the loss of valence electrons (e.g., 4d/5s electrons) reduces electron shielding, increasing the effective nuclear charge. This strengthens the 1s electron binding energy, thereby raising the energy required for 1s→4p transitions and shifting the absorption edge to higher energies. Our review of the pertinent literature also indicates that the Ru edge shift is frequently correlated with an increase in the oxidation state (Ref. 29, 41, 47).

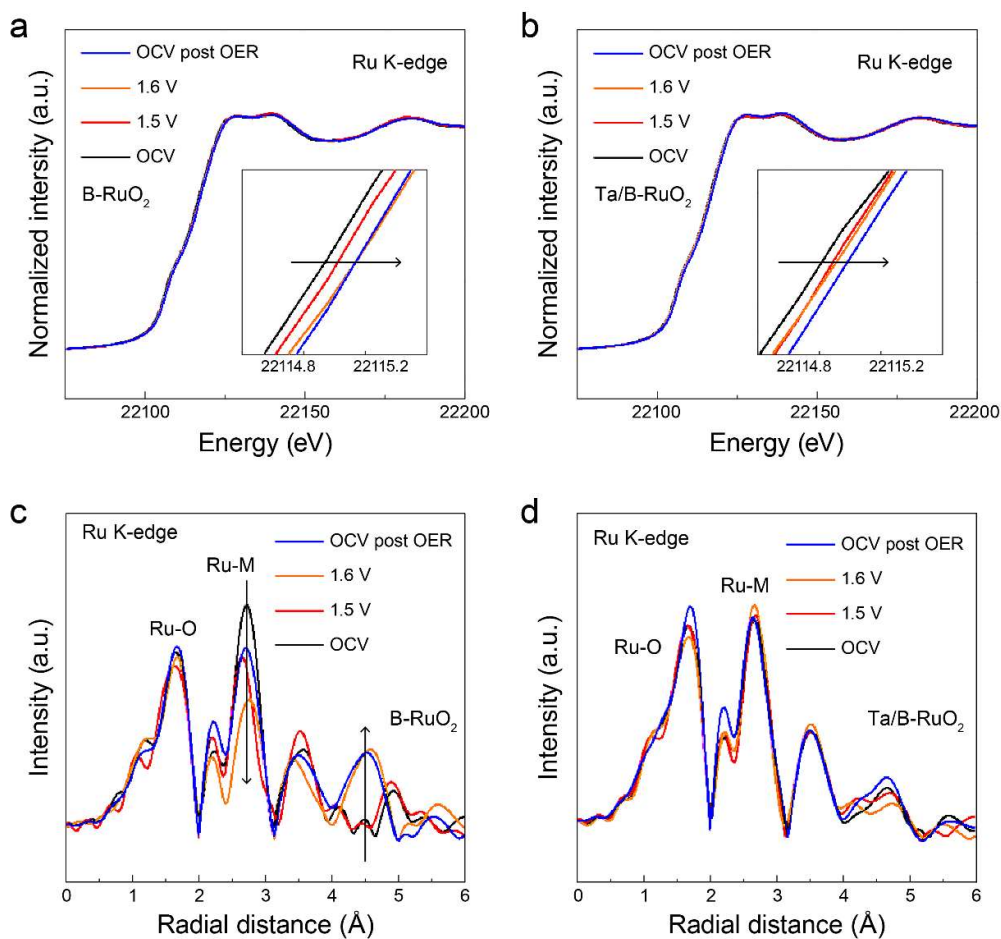


Figure R11. (a, b) Operando Ru K-edge XANES analyses of B-RuO₂ and Ta/B-RuO₂ at various biases. (c, d) The corresponding Ru K-edge FT-EXAFS spectra.

Additionally, Ta/B-doped RuO₂ exhibits a hierarchical porous structure (Figure R12). Although the ligament length of the nanopores is small, the surface atoms represent a relatively modest proportion of the total atoms. This feature results in relatively minor changes in the spectral shapes of the Ru and Ta edges.

Our in situ XAS investigation primarily focused on the role of Ta in suppressing the increase in Ru oxidation state and its dissolution, a conclusion that is strongly supported by our experimental data. We fully agree on the importance of comparing our experimental material with commercial RuO₂ to better highlight the effects of Ta doping. However, due to the tight availability of XAS beamtime, we are currently unable to schedule this comparative study within the specified timeframe. We apologize

for this limitation and plan to conduct more detailed investigations in future research to further enhance our understanding of this issue. We sincerely appreciate your understanding.

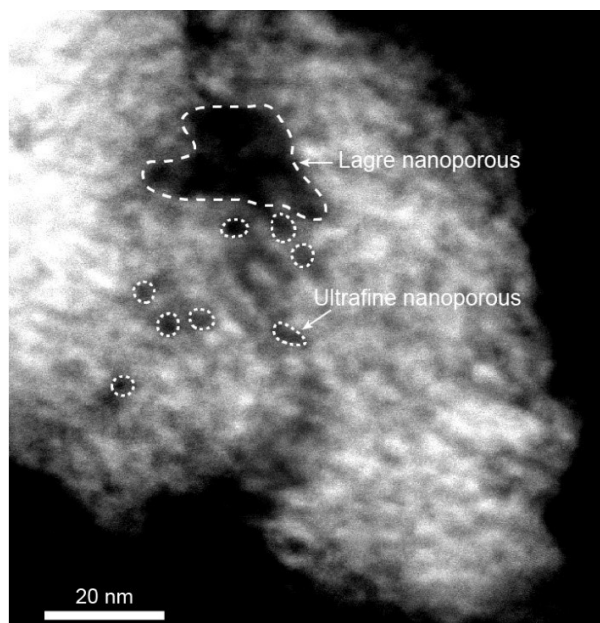


Figure R12. HAADF-STEM image of Ta/B-RuO₂.

Ref. 29: Liu, Y. et al. Ultrathin and Conformal Depletion Layer of Core/Shell Heterojunction Enables Efficient and Stable Acidic Water Oxidation. *J. Am. Chem. Soc.* **146**, 26897-26908 (2024).

Ref. 41: Deng, L.-M. et al. Valence Oscillation of Ru Active Sites for Efficient and Robust Acidic Water Oxidation. *Adv. Mater.* **35**, 2305939 (2023).

Ref. 47: Shi, Z.-P. et al. Customized reaction route for ruthenium oxide towards stabilized water oxidation in high-performance PEM electrolyzers. *Nat. Commun.* **14**, 843 (2023).

9. The FT-EXAFS data can be improved. Specifically, the intensity at 1 Å and below do not have any physical meaning, so the intensity should be at 0 there. The authors need to properly discuss the changes they see. If Ru-M does not change, why Ta-M is changing?

Reply: We sincerely appreciate the reviewer's insightful comments and valuable suggestions.

In EXAFS spectroscopy, data below 1 Å in the Fourier-transformed R-space are considered non-physical due to inherent limitations:

Physical mechanism: The short photoelectron wavelength at high k-values reduces scattering amplitude and invalidates the single-scattering approximation. Phase shift corrections further shift peaks by ~0.3-0.5 Å, making sub-1 Å peaks artifactual.

Data processing: Fourier transform truncation and window functions amplify noise and distort low-R signals, while the limited k-range (3-12 Å⁻¹) restricts resolution.

Atomic scale: Most chemical bonds exceed 1 Å, and ultra-short distances (e.g., in H₂) are rarely probed

by EXAFS due to signal overlap and experimental constraints.

Instrumental noise: Detector artifacts and background fluorescence dominate the low-R region.

Thus, EXAFS analysis focuses on $R > 1 \text{ \AA}$, with sub- $1 \text{ \AA}$ features dismissed as noise or processing artifacts. Although data with $R < 1 \text{ \AA}$ typically do not directly correspond to physical structures, their retention is a necessary step in the EXAFS analysis procedure (**Ref. 48**). This approach is aimed at ensuring the rigor of the mathematical processing and avoiding information loss.

During the OER process, Ta undergoes significant structural transformations. Specifically, Ta has been shown to effectively mitigate the over-oxidation and dissolution of Ru by modulating its electronic and atomic structures. However, in the Ta/B-RuO₂ composite, the atomic ratio of Ru to Ta is considerably higher. Only a minor fraction of Ru's overall coordination environment is influenced by the presence of Ta. Consequently, in the Ta/B-RuO₂ system, the extent of changes observed in Ru-M is significantly smaller than that in Ta-M. We have incorporated this detailed discussion into the manuscript. Thank you once again for your valuable suggestion.

Ref. 48: Wang, Y. et al. Mesoporous Single-Crystalline Particles as Robust and Efficient Acidic Oxygen Evolution Catalysts. *J. Am. Chem. Soc.* **147**, 13345-13355 (2025).

10. Raman spectra does not seem to be identical, despite the authors' phrase: "In contrast, the consistent Raman signal observed for Ta/B-RuO₂ indicated that its crystal structure remains remarkably stable under OER conditions". Please, revise this part.

Reply: We are deeply grateful to the reviewer for their insightful recommendation. Based on the reviewer's suggestions, we have revised the description in the manuscript. The adjustment highlights that, compared to B-RuO₂, the Raman signals of Ta/B-RuO₂ exhibit relatively small variations in the three characteristic peaks (E_g , A_{1g} , and B_{2g}) associated with the crystal structure (**Figure R13** and **Ref. 28**). This observation suggests a higher structural stability of Ta/B-RuO₂.

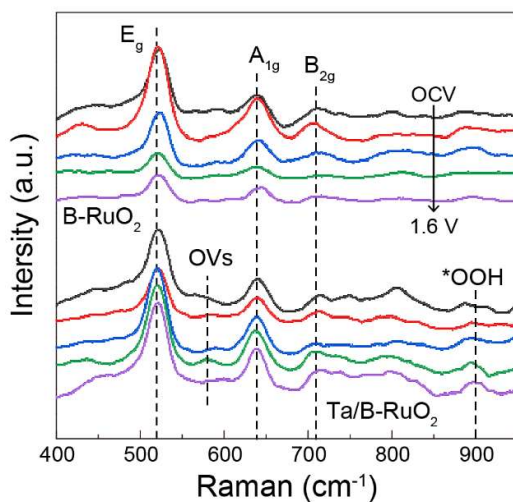


Figure R13. In-situ Raman spectra of Ta/B-RuO₂ at various biases.

Ref. 28: He, W.-D., et al. Grain-Boundary-Rich RuO₂ Porous Nanosheet for Efficient and Stable

11. DEMS results presented in Figure 4 are missing the error bars.

Reply: We sincerely appreciate your insightful suggestion. As depicted in **Figure R14**, error bars have been added to the figure, thereby offering a more detailed and accurate depiction of the results.

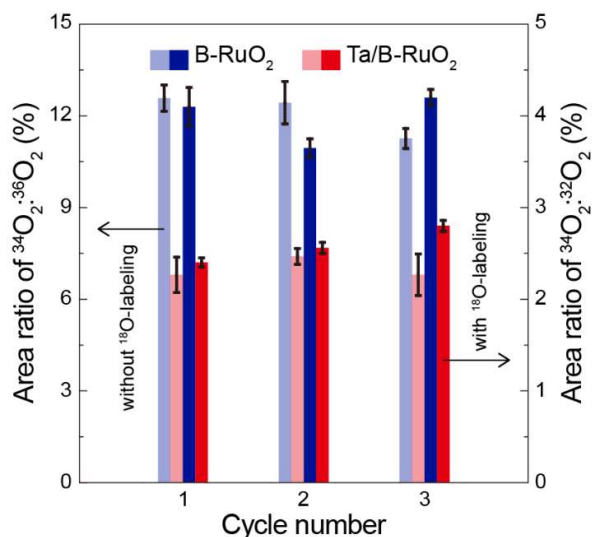


Figure R14. The peak area ratio of $^{34}\text{O}_2/^{32}\text{O}_2$ and $^{34}\text{O}_2/^{36}\text{O}_2$ of B-RuO₂ and Ta/B-RuO₂.

Reviewer #3:

For the theoretical section, the authors performed standard first-principles calculations to investigate the OER performance of boron-tantalum co-doped RuO₂. However, the computational methodology lacks rigor, and the following suggestions are provided for improvement:

Reply: We sincerely thank the reviewer for their insightful suggestions, which have been instrumental in improving the quality of the manuscript. Based on the reviewer's recommendations, we have carefully revised the relevant content to better address the issues raised and enhance the overall clarity and accuracy of our work.

1. Lack of references in the computational details. Please cite relevant literature to validate the methodology.

Reply: We are grateful for the constructive suggestions offered by the reviewer and sincerely apologize for the oversight. In the revised manuscript, we have meticulously reviewed and incorporated relevant literature.

Ref. 49: Car, R. et al. Unified Approach for Molecular Dynamics and Density-Functional Theory. *Phys. Rev. Lett.* **55**, 2471 (1985).

Ref. 50: Jones, R. O. et al. The density functional formalism, its applications and prospects. *Rev. Mod. Phys.* **61**, 689 (1989).

Ref. 51: Kresse, G. et al. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169 (1996).

Ref. 52: Hammer, B. et al. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Phys. Rev. B* **59**, 7413-7421 (1999).

Ref. 53: Perdew, J. P. et al. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865 (1996).

2. As shown in Figure S18, the slab model appears to lack fixed atomic layers, which may lead to unrealistic surface relaxation during optimization. To ensure stability, it is standard practice to immobilize the bottom 2-3 layers. Please revise the model accordingly.

Reply: We appreciate the reviewer's suggestion. After further discussions with our collaborating colleagues and a careful re-examination of our model, we have confirmed that the bottom two layers were indeed already immobilized.

3. In Figure 5a, what is the isosurface value of electron gas in charge density difference? What did the color represent?

Reply: We are grateful for your insightful suggestions. In **Figure 5a**, the charge density difference is visualized using an isosurface threshold of $0.01 \text{ e}/\text{\AA}^3$. Following the standard convention for charge redistribution plots, yellow regions indicate electron density accumulation, while blue regions correspond to electron depletion. The corresponding description has been incorporated into the manuscript.

4. How were the B/Ta doping sites determined? A systematic comparison of different sites and their formation energies are needed

Reply: We appreciate the reviewer's reminder. We have included the results of the formation energy calculations for various doping sites in the supplementary information (**Figure R15**). Concurrently, we have incorporated a detailed discussion regarding the confirmation of doping sites into the relevant sections:

Considering that B atoms are oxidized during the preparation and OER processes, they are expected to coordinate with O atoms to form a BO_2 structure. DFT calculations were employed to investigate the possible doping models of B and Ta atoms in RuO_2 , specifically focusing on the Ru-cus and Ru-bri sites. The calculated energies were utilized as a criterion for assessing the thermodynamic stability of B and Ta doping. Among these models, the Ru-bri site exhibited the lowest energy for B doping, while the Ru-cus site demonstrated the lowest energy for Ta doping.

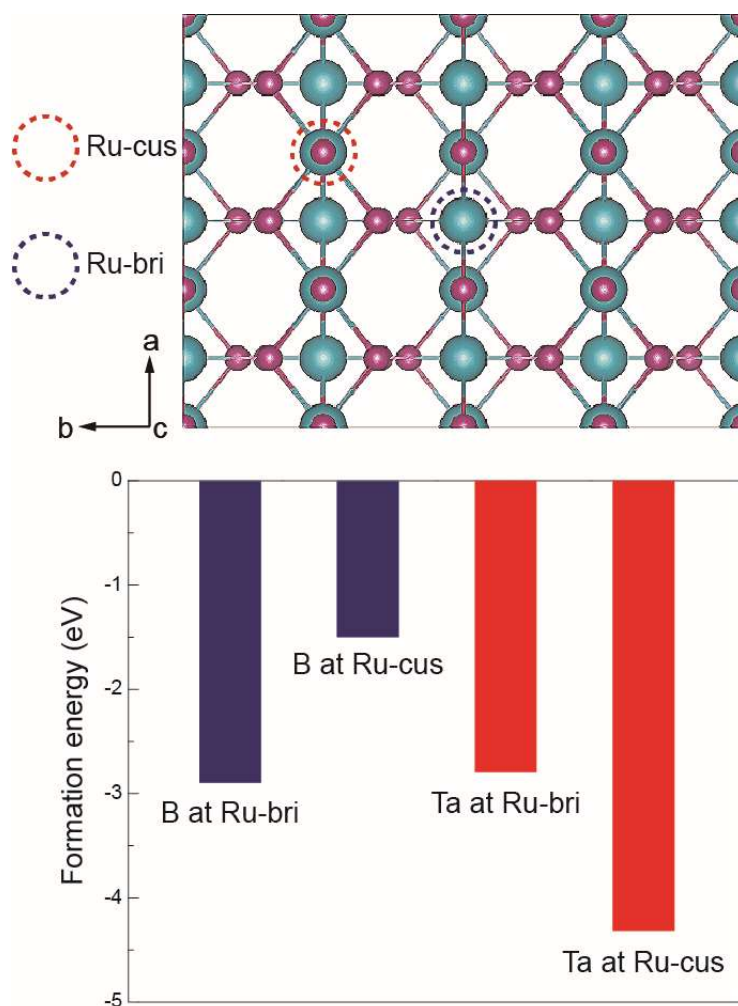


Figure R15. Formation energies of B and Ta doped at different sites.

5. In Figure 5c and 5d, how about the hybridization between O/B p -orbital and Ru d -orbital?

Reply: Many thanks for the reviewer's helpful suggestions. We have added the PDOS analysis and related discussions to the manuscript.

DOS and PDOS analysis revealed that the introduction of Ta and B dopants generates novel hybridized electronic states (**Figure R16**). Specifically, B doping significantly enhances the hybridization between O $2p$ orbitals and Ru $4d$ orbitals near the Fermi level, which increases the density of occupied Ru $4d$ states critical for OER charge transfer. Upon co-doping with Ta and B, the density of occupied Ru $4d$ states shows further enhancement. Crucially, Ta doping induces direct O $2p$ -Ta $5d$ orbital interactions that activate Ta atoms by increasing the density of accessible Ta $5d$ states near the Fermi level. The synergistic coupling between B-mediated Ru site activation and Ta $5d$ state modulation collectively enhances the catalytic activity beyond individual doping effects.

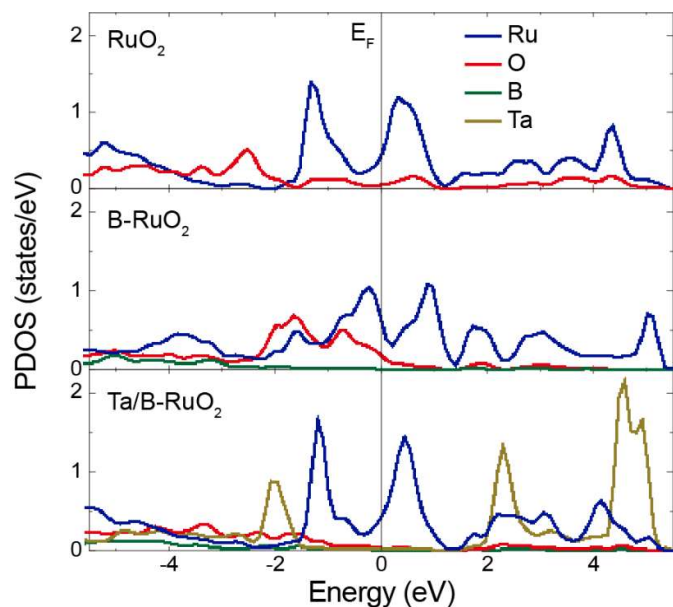


Figure R16. PDOS of RuO₂, B-RuO₂, and Ta/B-RuO₂.

6. In Figure 5e, the authors mentioned the gap between Ru *d*-orbital and O *p*-orbital. Please provide more explanation. How about the B element?

Reply: We sincerely appreciate your valuable suggestion. We have accordingly supplemented the content of this section to provide a more comprehensive analysis.

Moreover, the widening of the gap between Ru *d* orbitals and O *p* orbitals in Ta/B-RuO₂ can be attributed to the dual functionality of Ta as an electron donor and a structural modulator. Specifically, Ta doping induces electron transfer to Ru, which in turn lowers the Ru *d*-band center and concurrently polarizes the O *p*-band. This electronic decoupling suppresses LOM by elevating the energy barrier for O diffusion, thereby redirecting the OER pathway toward the AEM. Concurrently, the larger atomic radius of Ta introduces lattice strain, which restricts O mobility and stabilizes the RuO₂ framework. These synergistic effects collectively enhance the overall durability of the material. This result can also be corroborated through the analysis of the PDOS (**Figure R16**).

We elucidate the effect of B doping through the analysis of the PDOS (**Figure R16**). B doping induces an electronic interaction with O atoms, which in turn indirectly enhances the hybridization between the O *p* orbitals and the Ru *d* orbitals.

7. In Figure 5g, B-doping is absent in B-RuO₂ whereas B/Ta RuO₂ shows B doping in the bottom layer. Why?

Reply: Thank you very much for your reminder. The issue arises from an oversight in the illustration. Both models indeed feature B atoms doped at the bottom layer; however, these atoms were not clearly visible due to the occlusion by other atoms in the original view. To provide greater clarity, we have added a schematic diagram of the model from another angle, highlighting the positions of the doped B

atoms (**Figure R17**).

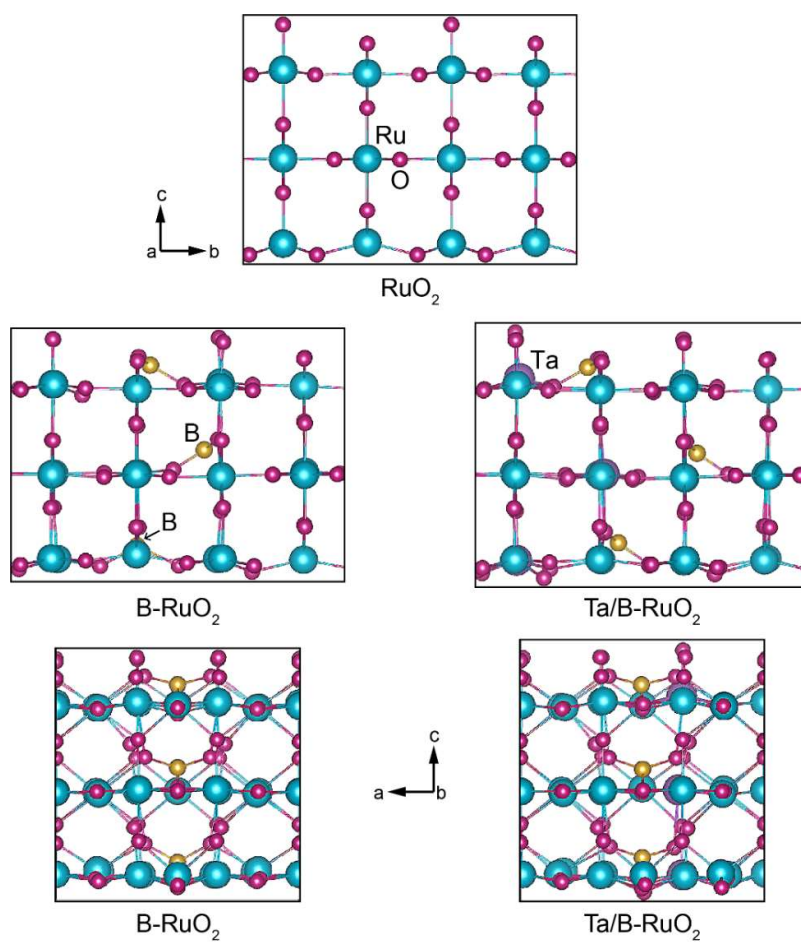


Figure R17. Models of RuO_2 , B-RuO_2 , and Ta/B-RuO_2 for DFT calculations.