

Peer Review File

Effect of ionic-bonding d⁰ cations on structural durability in barium iridates for oxygen evolution electrocatalysis



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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

In this work, Sim et al synthesized a series of BaIr-mixed oxides, using several TMs as doping agents. The authors reported that the introduction of certain cations induced a different ordering of [IrO_x] units in the doped material. In particular, the authors state that the introduction of Nb⁵⁺ or Ta⁵⁺ result in enhanced durability during the OER in acidic electrolyte. The authors ascribed this effect to the suppression of the lattice oxygen mechanism as a result of the more stable connectivity between the [Ir₃O₁₂] provided by the non-soluble cations. This is indeed an interesting line of research. As stated by the authors, several works in the literature already indicate that face-sharing iridates tend to display higher durability during the OER than other iridates with less degree of connectivity.

It appears as if pure samples were obtained for all iridates, without the presence of impurity phases or vacancies, and the with stoichiometry reported for each sample, is this correct?

The authors have performed a very interesting and insightful microscopy analysis of the fresh samples, showing the periodic arrangement of the cations in the samples. In my opinion, the same study should have been conducted for the used samples, at least for the ones containing Nd or Ta cations. Such a study would allow to prove the stability of such cations in the iridate networks during the OER. In turn, this would further support the hypothesis that the reaction pathway (if actually happening) accounts to the stabilization of the IrO_x trimers. Also, focusing not only on the bulk structure of the materials, but also on the surface composition/evolution, would have been desirable.

OER activity/stability trends are shown in Figure 3. What is the unit of A/F initial? Except, perhaps, for BaIrO₃, all other catalysts fail to show stable activity. Clearly, either an increase or a decrease of activity is observed during the first cycles. For instance, the OER activity (assuming that A/F represents the OER activity of the catalyst) increases by a factor of 3 during the first 200 cycles for the Nb sample, suggesting lack of stability. In all cases, this observation of an increasing or decreasing in activity, usually indicates a reconstruction of the surface (or even the bulk) of the catalyst (further supported by the evolution of the double layer capacitance). This feature should be studied in more detail since this is actually the most relevant feature of this work. In particular, studies should be focused on determining the evolution of the catalyst(s) surface by focusing on surface sensitivity analyses and/or study of the dissolution of cations. Determining surface composition by EDS might not be fully accurate since this is not a surface sensitive technique. In addition to showing EELS for Ir and Nb, Ta etc, other analysis such as XPS could provide suitable information concerning the evolution of the surface concentration of Nb/Ir.

As for the measurement of the double layer capacitance, I wonder if the authors have used a carbon-containing ink for the deposition of the catalysts.

Finally, how does the activity and durability of the catalysts reported in this work compares against the literature, specially of iridates? OER polarization curves should be shown, at least in the supplementary information section.

Reviewer #2 (Remarks to the Author):

The authors present the synthesis and comprehensive characterization of barium iridates substituted

with different (post-)transition metal elements as electrocatalysts for the oxygen evolution reaction (OER). They show that different substituents lead to different crystal structures with structural motifs of different inherent stability. Moreover, they show that the ionicity of Nb-O and Ta-O bonds strongly stabilized the materials, resulting in long-term stable catalytic performance.

These results will be of high relevance for the future synthesis of catalysts that are stable under acidic conditions while reducing the amount of iridium atoms. I believe the work to be carried out with sufficient care and recommend reconsidering the manuscript after the authors have addressed the following comments:

- 1) The authors show a sketch in Fig. S22 that is supposed to show the stability of the bridging site in the trimer unless all three O are removed simultaneously. What is the justification for this stability? I believe that additional DFT calculations could help in unraveling the stability at the surface in conjunction with the experiments.
- 2) Control experiments were performed with as-synthesized and ball-milled IrO₂ powders. How can it be excluded that the observed effects stem from impurities introduced during milling rather than the particle size as invoked by the authors?
- 3) In Fig 5g, what is the origin behind the XAS peak intensity variations?
- 4) How would DFT results change if spin configurations other than the low-spin were considered? Can the pDOS be reconciled with the experimental stability in all cases? Related to this, how was the magnetic order in the presence of Ir⁴⁺ treated? Calculations were spin-polarized but only one spin-channel is shown in the DOSs?
- 5) I have some issues with the nomenclature adopted by the authors. Even though the term "hexagonal perovskite" can be found in the literature, "perovskite" refers to a crystal structure with corner-sharing octahedra. Calling everything that has ABO₃ stoichiometry a "something" perovskite is therefore highly misleading (let's leave aside that the solar-cell community is starting to call everything that absorbs light a perovskite).
- 6) Another nomenclature issue is the use of "hybridization". This term refers to linear combinations of atomic orbitals on a given atom (i.e. sp² or sp³ hybridization of carbon atoms). What the authors refer to on the other hand are linear combinations of atomic orbitals between atoms, which is covalence rather than hybridization.
- 7) The terminology and language adopted by the authors do not make for easy reading. For example, "noncorrosive" refers to "corrosion resistant", "disconnection" to "bond breaking", "sustainability" to "long-term stability" or "molecular-level electron energy diagram" to "molecular orbital diagram". Adopting conventional terms will make the manuscript significantly more accessible.

Reviewer #3 (Remarks to the Author):

Sim et al. present a detailed study of Ir-based perovskites for the oxygen evolution reaction. Using advanced electron microscopy studies, SIMS and electrochemical measurements, they show how the structure of these materials changes as a result of the catalytic conditions. In the end, all reported materials turn into amorphous oxides at the surface (as is so often the case for Ir-based perovskites). For most materials, pure IrO₂ is formed. In some cases, IrNbO₂ or IrTaO₂ is formed. The authors show that the extra Nb and Ta has a stabilizing effect compared to pure IrO₂, in agreement with previous research (e.g. <https://pubs.acs.org/doi/10.1021/acsami.0c12609>). Overall, I find that although the work is carefully performed and reported structural evolution is well-documented, the novelty of the conclusions is limited. It does not, as is claimed, provide any fundamentally new strategy for improving catalyst stability. Therefore, I do not recommend publication in Nature Communications. That said, using the detailed comments below, I do believe that the manuscript could be made suitable for a more specialized journal.

1. The authors claim that Ir-based perovskites provide a platform for producing comparatively stable OER catalysts, because the IrO₆ octahedra are highly connected (more so than in e.g. rutile oxides). While I understand this argument, practice shows that it does not hold. In fact the authors show that all perovskites amorphize at the surface. After this amorphization, it is unlikely that the edge-sharing octahedra structure is preserved. Hence, the claim seems unjustified. Instead, I think the data from the authors shows once more that the electronic structure of the materials is much more important than their crystal structure (Nb and Ta manage to stabilize the oxide, even when an amorphous layer is formed).

2. Much of the analysis and arguments are based on the bulk structure of the perovskite. However, as discussed in the previous point, this is not useful when the electrode surface becomes amorphized. From this perspective, the lengthy TEM analysis of the bulk crystal structure could be moved to the SI in large part. Also, the DFT analysis in Fig. 5 becomes meaningless, because it assumed the bulk perovskite structure. It is not directly obvious that the Nb would have the same effect in amorphous IrNbO₂ formed once the Ba has left.

3. It would be good if the authors are a bit more specific in their description of the SIMS measurements. The SIMS method employed here to quantify the degree of lattice oxidation is not strictly measuring this quantity. What it measures is the depth in the sample to which lattice oxidation occurs. It does not provide a ratio between lattice oxygen evolution and the “regular” adsorbate evolution mechanism. It is important that the authors make this distinction for clarity.

4. The degradation of the pure IrO₂ samples reported by the authors is much too fast to be related to dissolution of IrO₂. It seems likely that particle detachment plays an important role here, which is mostly due to the method for depositing the catalyst particles rather than their intrinsic properties.

5. Fig. 1: Ir and O are both labelled grey in the crystal structures. This makes it them very difficult to interpret.

6. Fig. 3: It is not clear to me how the current density is defined here. At what potential is the OER activity measured? How is the capacitance used for the normalization defined? I think it is important that the authors note that such a normalization by capacitance does not necessarily yield a fair comparison of current densities between the materials, because the capacitance per unit surface area likely differs for the different materials. And can the authors exclude the possibility of degradation due to

particle detachment during OER (which is not an intrinsic material property, but rather a function of how the catalyst was deposited on the substrate)?

7. The labeling of the O K-edge spectra is a bit over-simplified. Since Ir is not the only metal in the material, it is not certain that the resonances in the O K-edge between 528 and 533 eV can all be attributed to Ir-O hybridized empty states. In fact, most metal oxides show resonances in this range.

Hence, Ba-O and Nb-O resonances will likely be present here as well.

8. SI Figure 23: O1s increases instead of decreasing (which the caption says it should do). Was something mislabeled?

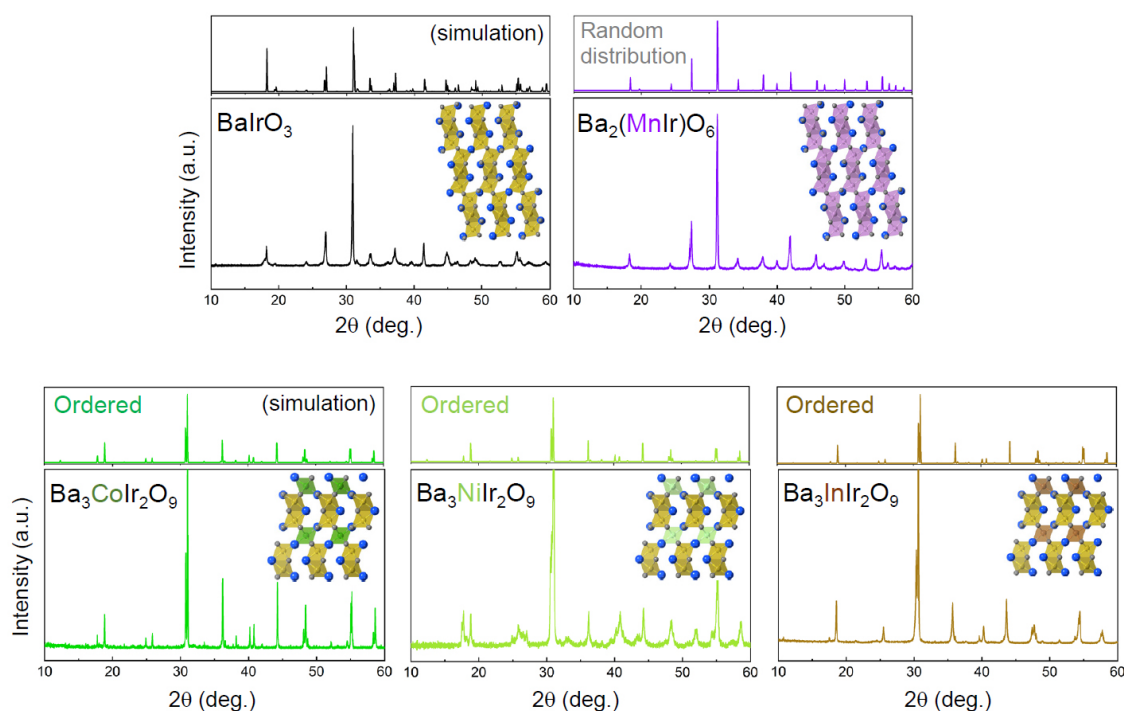
Responses to Comments of Reviewer #1 on NCOMMS-23-53106-T

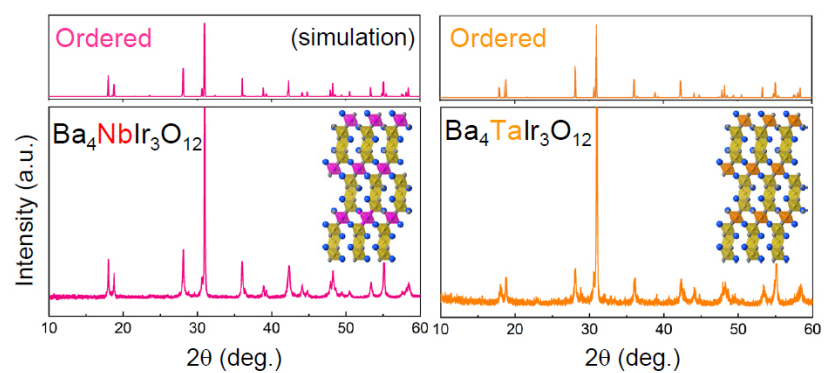
(General Comment) In this work, Sim et al synthesized a series of BaIr-mixed oxides, using several TMs as doping agents. The authors reported that the introduction of certain cations induced a different ordering of $[\text{IrO}_x]$ units in the doped material. In particular, the authors state that the introduction of Nb^{5+} or Ta^{5+} result in enhanced durability during the OER in acidic electrolyte. The authors ascribed this effect to the suppression of the lattice oxygen mechanism as a result of the more stable connectivity between the $[\text{Ir}_3\text{O}_{12}]$ provided by the non-soluble cations. This is indeed an interesting line of research. As stated by the authors, several works in the literature already indicate that face-sharing iridates tend to display higher durability during the OER than other iridates with less degree of connectivity.

(Re) We gratefully acknowledge the precise recognition of Reviewer #1 regarding what we have attempted to ascertain through a combination of atomic-level observations using electron microscopy, and electrochemical and spectroscopic measurements. His or her relevant comments lead us to believe that the reviewer must have long-term experience in electrocatalysis as well as structural chemistry for energy conversion. The reviewer made several important comments along with kinds suggestions for revision. Our responses to the comments and appropriate modifications are provided below.

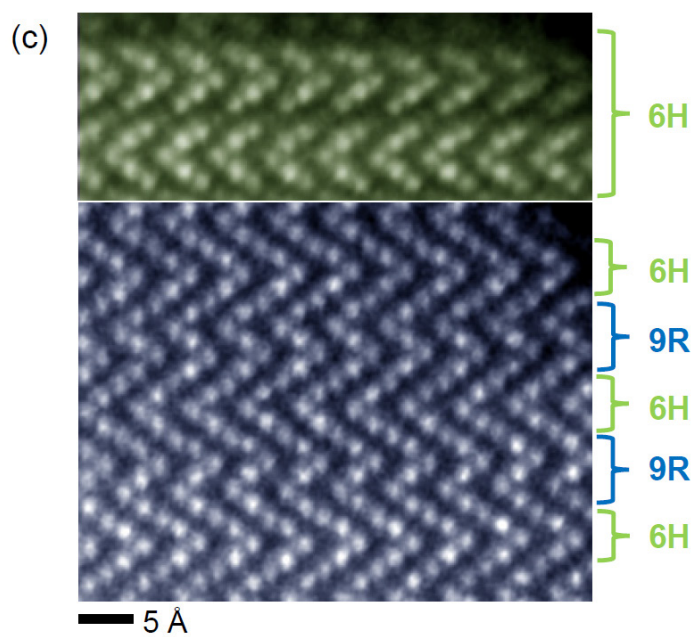
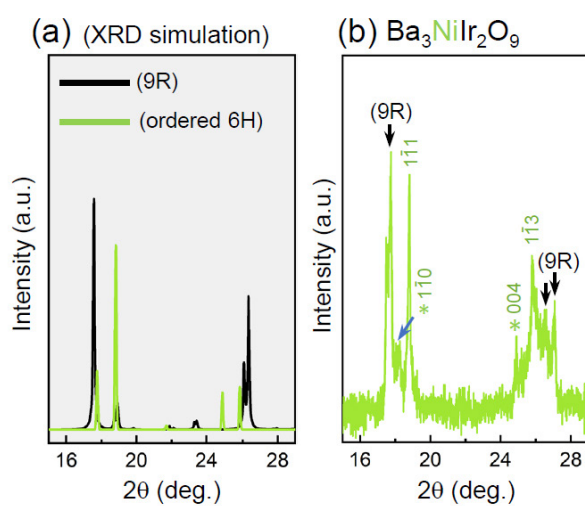
(Comment #1) It appears as if pure samples were obtained for all iridates, without the presence of impurity phases or vacancies, and the with stoichiometry reported for each sample, is this correct?

(Re) As demonstrated in Supplementary Fig. 3 (see the following figure) in our manuscript, our XRD analyses confirm the absence of additional Bragg peaks corresponding to impurity phases. This finding further supports the stoichiometry of each of our samples. Additionally, the presence of the disordered 9R phase in the case of Ni-doped sample is directly verified, as demonstrated in the following HAADF image (Supplementary Fig. 6 in our revised version of the manuscript).



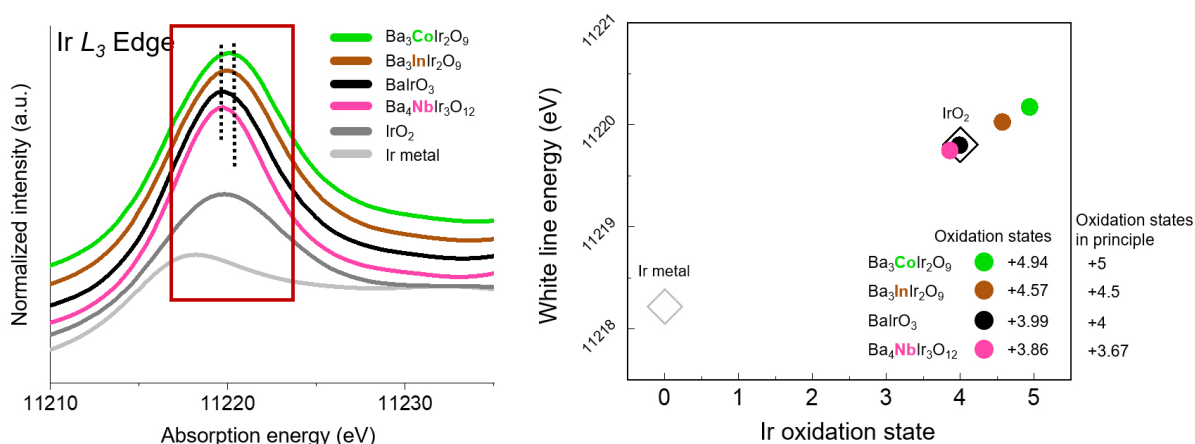


Supplementary Fig. 3



Supplementary Fig. 6

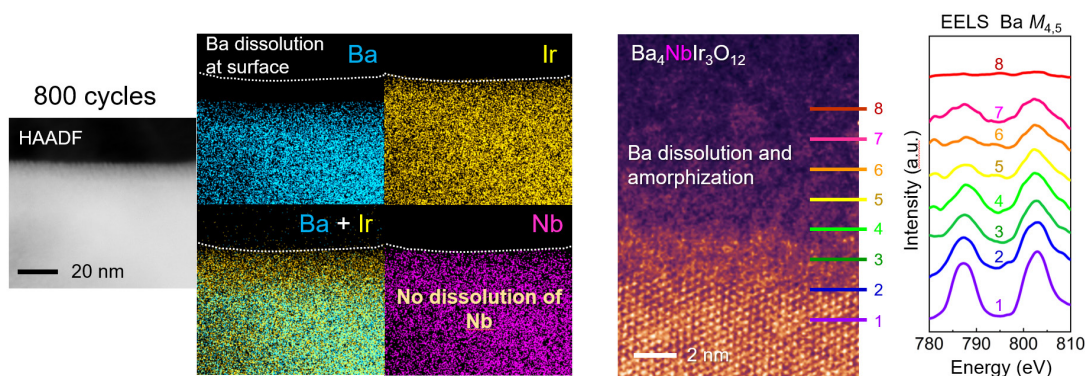
It is noted that the valence oxidation state of Ir will change to satisfy the overall charge neutrality condition when aliovalent dopant are added into BaIrO_3 . To precisely examine the oxidation state of Ir in Co^{2+} , In^{3+} , and Nb^{5+} -doped samples by comparing the relative positions of the Ir L_3 white lines among the samples, we have carried out X-ray absorption near edge structure (XANES) analyses. As shown below, each of the Ir oxidation states agree well with the value expected from the charge neutrality condition without additional vacancy formation. We have included these XANES results in Supplementary Fig. 8 in the revised version of our manuscript.

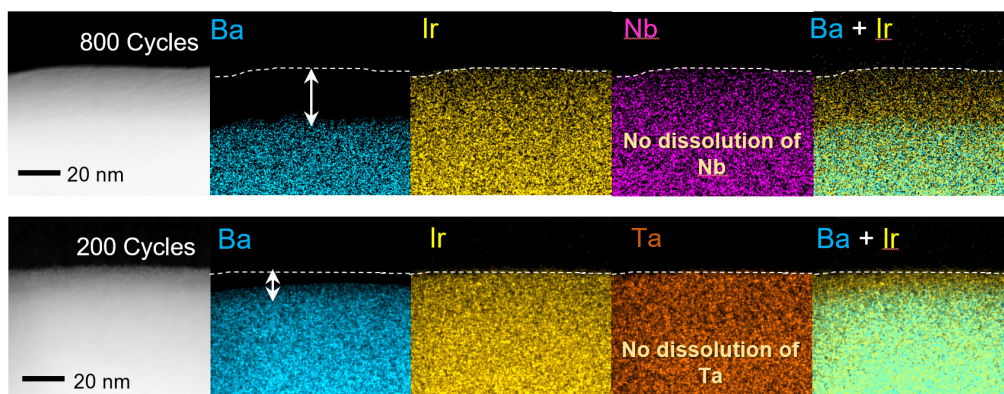


Supplementary Fig. 8

(Comment #2) The authors have performed a very interesting and insightful microscopy analysis of the fresh samples, showing the periodic arrangement of the cations in the samples. In my opinion, the same study should have been conducted for the used samples, at least for the ones containing Nb or Ta cations. Such a study would allow to prove the stability of such cations in the iridate networks during the OER. In turn, this would further support the hypothesis that the reaction pathway (if actually happening) accounts to the stabilization of the IrO_x trimers. Also, focusing not only on the bulk structure of the materials, but also on the surface composition/evolution, would have been desirable.

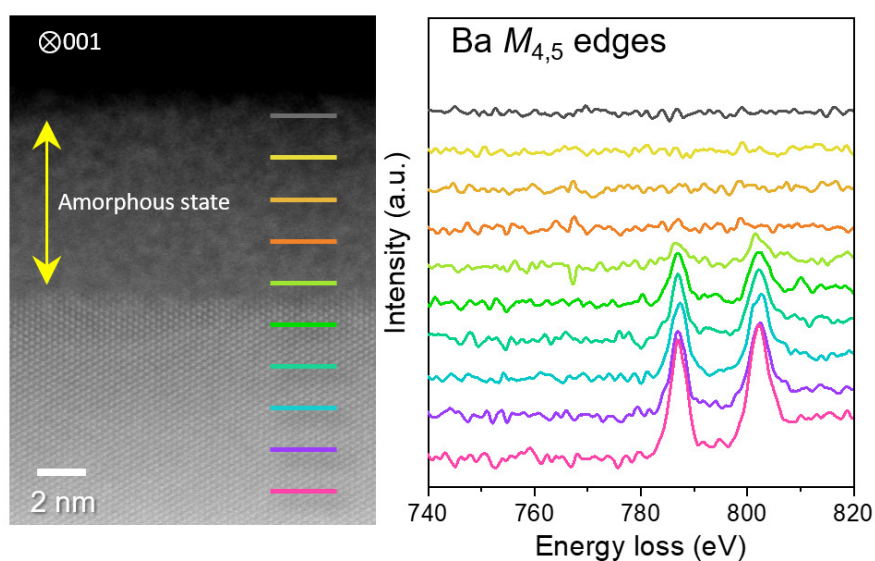
(Re) We definitely agree that the observation of post-OER samples is of great significance. As shown below, we thus scrutinized the surface of Nb-added particles after 800 cycles and provided the EDS and EELS results in Figures 4c and 4d in addition to Supplementary Figs. 17 and 18 in our original manuscript (now Supplementary Figs. 19 and 20 in the revised version).





Supplementary Figs. 19 and 20

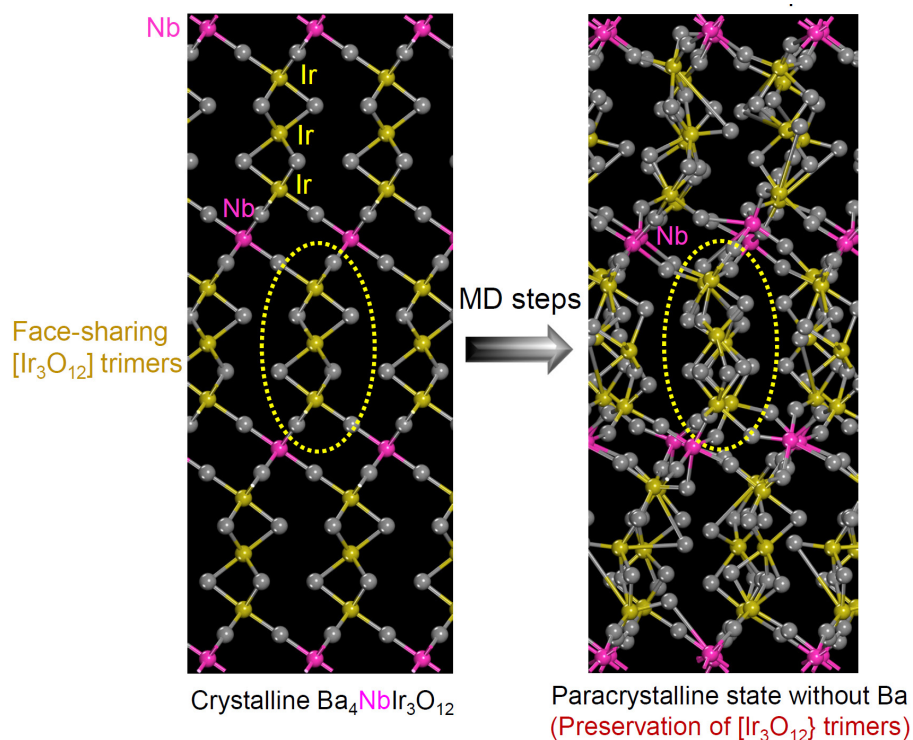
These nanoscale EDS maps and line-by-line EELS analyses directly demonstrate the Ba-deficient amorphous state at the surface of particles. As reported in previous studies (Song *et al.* “Dissolution-Induced Surface Roughening and Oxygen Evolution Electrocatalysis of Alkaline-Earth Iridates in Acid,” *Chem* **5**, 3243 (2019); Lee *et al.* “Oxygen Evolution Reaction Activity in IrO_x/SrIrO₃ Catalysts: Correlation between Structural Parameters and the Catalytic Activity,” *J. Phys. Chem. Lett.* **10**, 1516 (2019)), the dissolution of alkaline-earth elements, such as Sr and Ba, in complex iridates are responsible for inducing the surface amorphization. To clarify this observation, we have carried out additional EELS analyses and included their results along with an HAADF image in Supplementary Fig. 22 in our revised manuscript, as demonstrated in the following figures.



Supplementary Fig. 22

It is noted that atomic-column imaging in STEM is based on the channeling effect of an electron beam traveling through each atom. As a result, a column contrast is significantly reduced when the periodic array of atoms is perturbed by Ba leaching. Clarifying the position of each atoms in an amorphous material by using STEM is thus very challenging and beyond the scope of the present work. To further reasonably support the robust framework of face-sharing [Ir₃O₁₂] trimers in the 12R structure, we have carried out *ab initio* molecular dynamics (MD) simulation. The simulation has been performed by using a supercell without Ba at an elevated temperature, 1200 K, to realize the Ba leaching condition and accelerate the atom

displacements. As shown below, despite substantial perturbation from the original positions of atoms, the overall ordered configurations of the $[\text{Ir}_3\text{O}_{12}]$ trimers and Nb are clearly identified. This result thus demonstrates how stable the face-sharing octahedra are even in the amorphous state without a long-range order. We have included these *ab initio* MD simulation results in Supplementary Fig. 28 in addition to providing a video clip as Supplementary Movie 1 in our revised version of the manuscript.



(*ab initio* MD Simulation) Supplementary Fig. 28

(Comment #3) OER activity/stability trends are shown in Figure 3. What is the unit of A/F initial? Except, perhaps, for BaIrO_3 , all other catalysts fail to show stable activity. Clearly, either an increase or a decrease of activity is observed during the first cycles. For instance, the OER activity (assuming that A/F represents the OER activity of the catalyst) increases by a factor of 3 during the first 200 cycles for the Nb sample, suggesting lack of stability. In all cases, this observation of an increasing or decreasing in activity, usually indicates a reconstruction of the surface (or even the bulk) of the catalyst (further supported by the evolution of the double layer capacitance). This feature should be studied in more detail since this is actually the most relevant feature of this work.

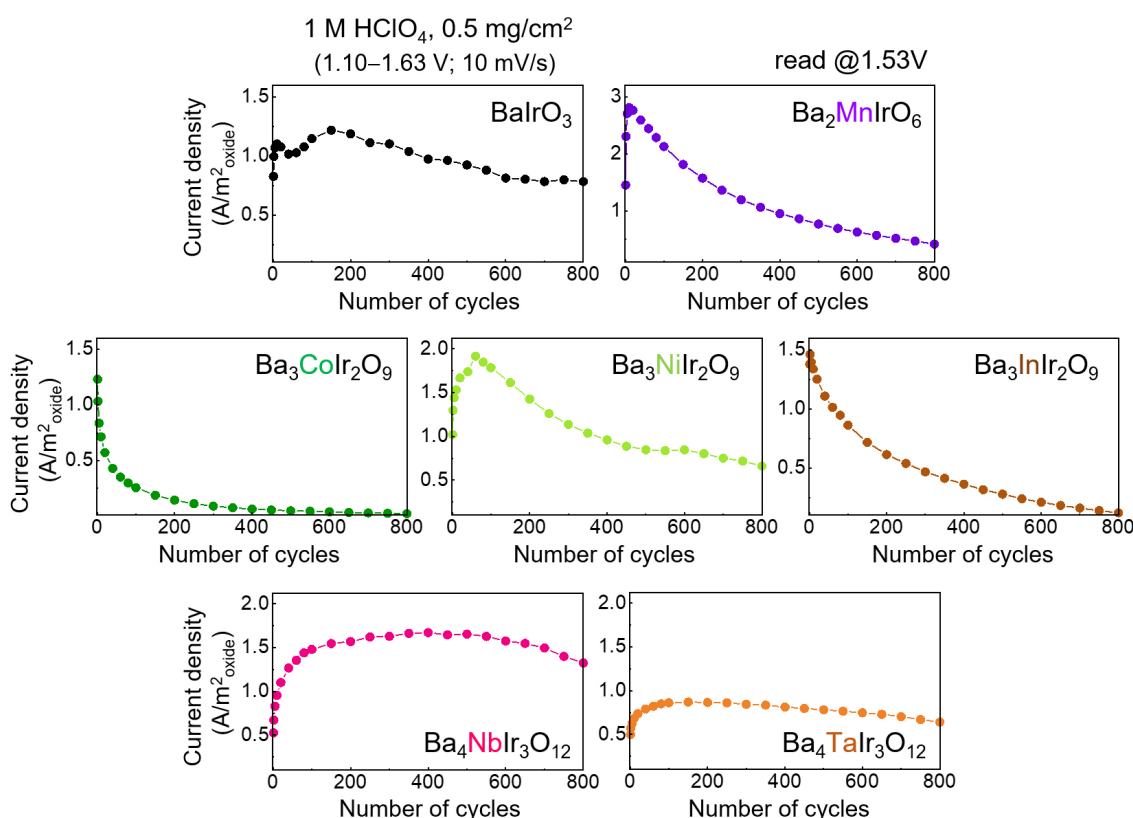
(Re) Yes, as mentioned by the reviewer, the unit, A/F (ampere per farad), represents the OER current density per unit surface area of a catalyst. Because the iridate materials used in this study exhibit different particle sizes, it is essential to compare samples based on an identical unit area for precise evaluation. In this regard, we measured double-layer (DL) capacitance to utilize these capacitance values as parameters representing the surface area of the catalysts. It is also worth noting that Ba leaching in BaIrO_3 induces significant surface roughening, as demonstrated in a previous study (Song et al. “Dissolution-Induced Surface Roughening and Oxygen Evolution Electrocatalysis of Alkaline-Earth Iridates in Acid,” *Chem* **5**, 3243 (2019)), leading to an increase in DL capacitance with anodic cycling. Therefore, we considered the initial value of capacitance to reflect the original surface area before the OER cycling tests

began and roughening occurred.

DL capacitance is commonly used to estimate the electrochemically active surface area (ECSA). Because this capacitance is measured in a non-faradaic potential range, it is strongly correlated with the surface area (McCroy *et al.*, *J. Am. Chem. Soc.* **135**, 16977 (2013)). ECSA is acquired from the following equation:

$$\text{ECSA} = C_{\text{DL}}/C_s$$

where C_{DL} is the measured DL capacitance of a catalyst material and C_s is the specific capacitance of the sample per unit area under a certain identical electrolyte condition. Specific capacitance has been measured for a variety of metal electrodes in acidic and alkaline solutions, with typical reported values ranging between $C_s = 0.015\text{--}0.110\text{ mF/cm}^2$ in acidic H_2SO_4 . In the study of McCroy *et al.*, they used a general specific capacitance of $C_s = 0.035\text{ mF/cm}^2$ in an acidic condition as a reasonable general value. Therefore, we have adopted this value for our specific capacitance ($C_s = 0.035\text{ mF/cm}^2$) and estimated the ECSA of each sample accordingly. To prevent any misunderstanding, we have revised our data in Figure 3 based on the ECSA suggested by McCroy *et al.*, as shown below, and have provided additional details regarding the ECSA in the Methods section in our revised manuscript for readers.

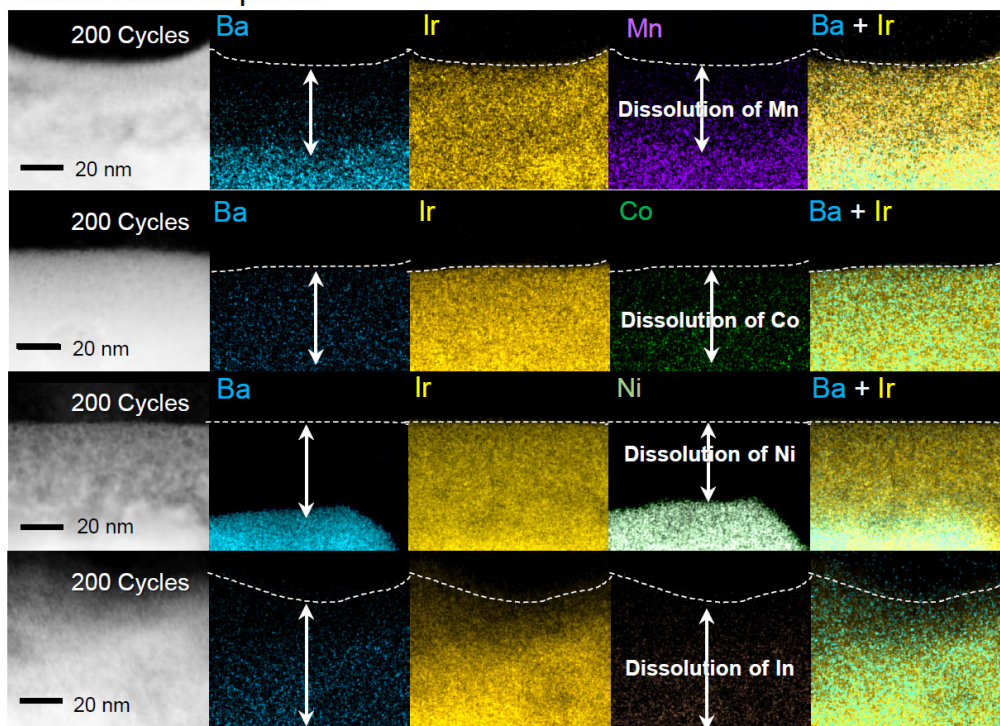


As addressed above, Ba dissolution and subsequent surface roughening in some BaIrO_3 samples result in the manifold increment in OER activity during the initial cycles. We thus note that the increasing activity, a positive feature for catalysts, is associated with neither structural instability nor failure to maintain stable activity. As shown in Figure 3 and explained in its caption, no degradation of activity is distinctively observed in the Nb- and Ta-doped samples, whereas the samples doped with Mn, Co, Ni, and In show a substantial decrease in the OER current with cycling.

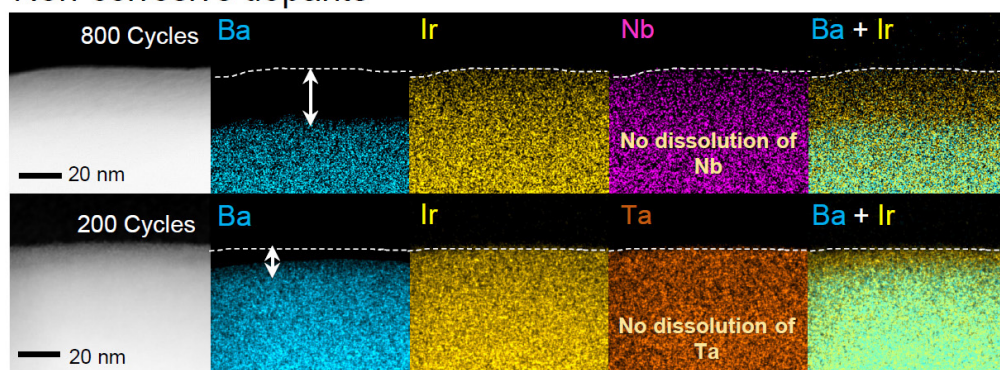
In addition to providing the DL capacitance variations of all the samples in Supplementary Fig. 24 in the manuscript, we clarified the surface structures and composition maps for all the

post-OER samples in Supplementary Figs. 14–20 for readers' better understanding. Based on these experimental results, we can classify our samples into two distinct groups; one pertains to the (Mn, Co, Ni, and In)-doped samples and the other is associated with the non-corrosive dopants (Nb and Ta). Typical examples showing the surface structures and composition variations after the OER are provided below for each group.

Dissolvable dopants



Non-corrosive dopants

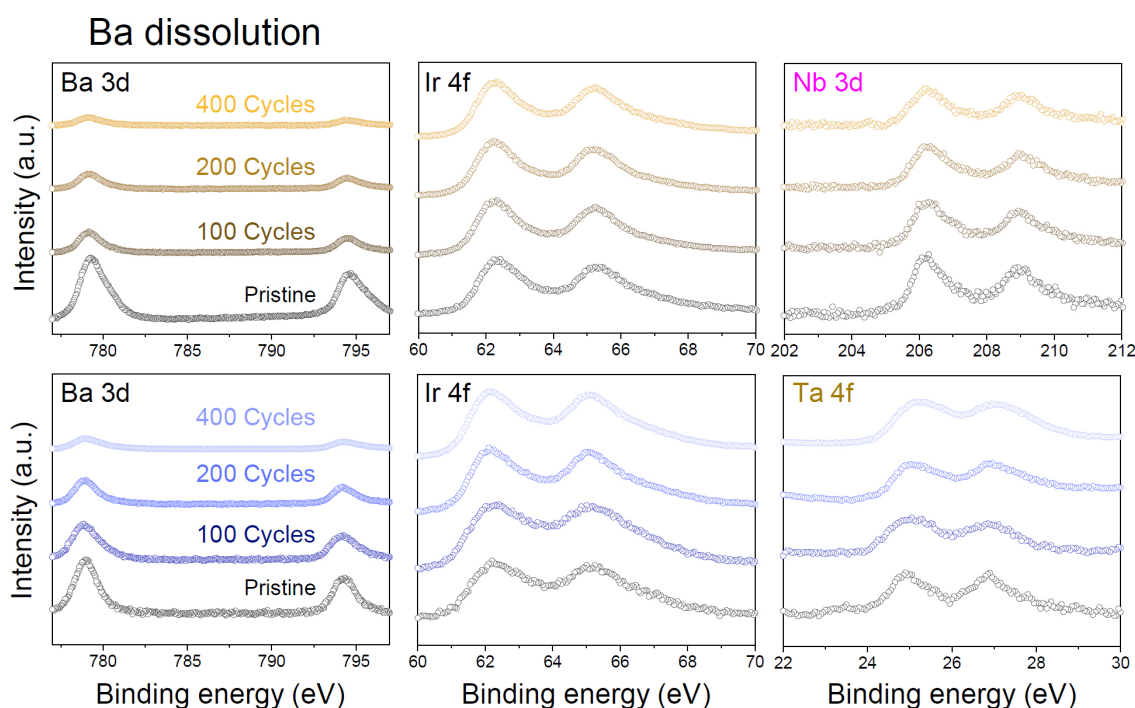


As is evident, Mn, Co, Ni, and In are highly corrosive in acidic conditions, making their avoidance of dissolution into an electrolyte challenging. From a structural perspective, the face-sharing $[\text{Ir}_2\text{O}_9]$ dimers in the 6H type would readily disconnect if the dopant cations at the bridging sites dissolve rapidly. Although Mn is randomly distributed within the $[\text{Ir}_3\text{O}_{12}]$ trimers in the 9R type, it shows similar disruptive behavior, thereby compromising the $[\text{Ir}_3\text{O}_{12}]$ -trimer framework. Consequently, lattice collapse and decomposition, arising from the dissolution of both Ba and the dopants, become inevitable. This results in the reduction of DL capacitance (due to particle decomposition) as shown Supplementary Fig. 24 and the development of a significantly porous structure in the surface region of post-OER particles containing Mn, Co,

Ni, and In, as demonstrated in Supplementary Figs. 15–18. In stark contrast, as evidenced by the Pourbaix diagrams, Nb and Ta show notable resistance against electrochemical corrosion in acid. Therefore, despite the easy dissolution of Ba, the $[\text{Ir}_3\text{O}_{12}]$ trimers and their interconnection bridged by Nb and Ta remain relatively undisturbed during the OER. As shown above, our *ab initio* MD simulation consistently supports this structural robustness of the 12R type.

(Comment #4) In particular, studies should be focused on determining the evolution of the catalyst(s) surface by focusing on surface sensitivity analyses and/or study of the dissolution of cations. Determining surface composition by EDS might not be fully accurate since this is not a surface sensitive technique. In addition to showing EELS for Ir and Nb, Ta etc, other analysis such as XPS could provide suitable information concerning the evolution of the surface concentration of Nb/Ir.

(Re) We acknowledge that additional supportive surface analysis would strengthen our observations. In response to the reviewer's suggestion, we have carried out XPS analyses and incorporated the results into Supplementary Fig. 21 in the revised version of our manuscript. These findings confirm the dissolution of Ba and indicate no significant variation of Nb and Ta, which aligns with the results of the EDS and EELS analyses.



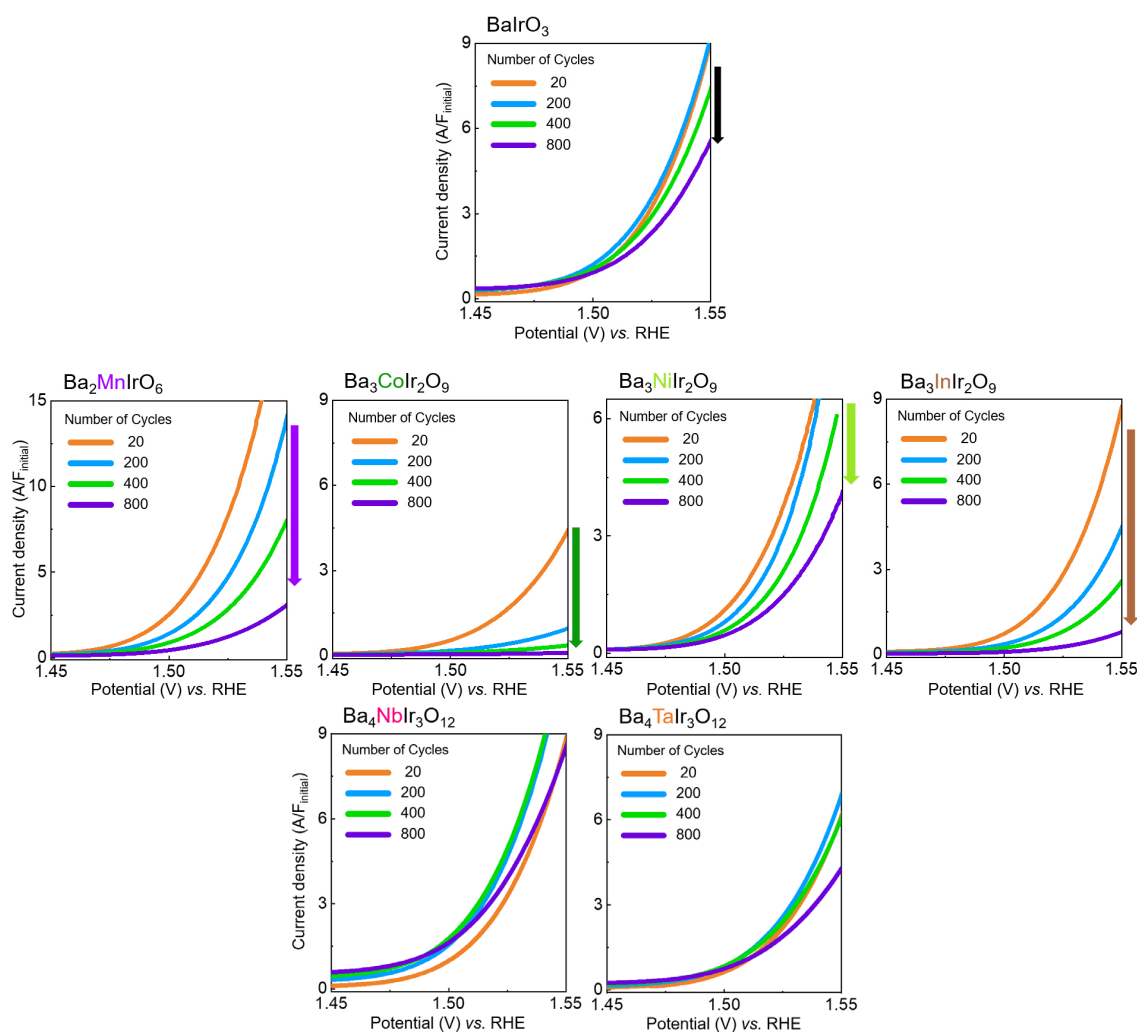
(Comment #5) As for the measurement of the double layer capacitance, I wonder if the authors have used a carbon-containing ink for the deposition of the catalysts.

(Re) Yes, we prepared our inks using catalyst particles, a 5-wt% Nafion solution (Nafion 117, Sigma-Aldrich) as a binder, and acetylene black (Alfa Aesar), along with high-purity ethyl alcohol. The mass ratios were adjusted to be 10:1 for the catalyst to acetylene black. Although BaIrO_3 is known to be metallic, the addition of a small amount of acetylene black is necessary to effectively reduce the inter-particle contact resistance in each sample. All the details are

provided in the Methods section for readers' reference.

(Comment #6) Finally, how does the activity and durability of the catalysts reported in this work compares against the literature, specially of iridates? OER polarization curves should be shown, at least in the supplementary information section.

(Re) Previous studies (Song *et al.*, *Energy Environ. Sci.* **13**, 4178 (2020); Guan *et al.*, *Adv. Mater.* **33**, 2103392 (2021)) have demonstrated that the durability of complex oxides, composed of face-sharing octahedra, is notably distinct alongside their high catalytic activity. Both studies verify that the high connectivity, based on sharing three oxygen atoms between adjacent oxygen octahedra, is a key structural geometry enhancing the overall stability of oxides. Given that the starting material of our study is the face-sharing hexagonal-perovskite BaIrO_3 , the effect of various dopants on the materials' durability can be directly compared. One significant finding in our work is that a complex iridate, $\text{Ba}_4\text{NbIr}_3\text{O}_{12}$, shows exceptional durability together with high OER activity. While Co, Ni, and In are found to readily dissolve into an electrolyte at pH = 0, Nb and Ta remain undissolved even after 1000 anodic cycles, thereby notably preserving the basic structural framework without lattice collapse. Following the suggestion of the reviewer, we have included the OER I-V curves for all the samples in Supplementary Fig. 11 for readers, as shown below.



Supplementary Fig. 11

All the additions and corrections in the text have been highlighted in blue in the revised manuscript. New sets of analysis results, along with further additions and DOS plots, have been included in Figure 5f, Supplementary Figures 8, 9, 11, 21, 22, 27, 28, 29, 32, and 34, as well as Supplementary Movie 1.

We have modified the title of this manuscript to “Effect of ionic-bonding d^0 cations on structural durability in barium iridates for oxygen evolution electrocatalysis” to specify the main claim of our work for readers’ better understanding.

It is quite apparent from his or her impressive review report that the reviewer has a broad spectrum of knowledge, not only on the subject of electrocatalysis. We sincerely appreciate the reviewer’s valuable suggestions and recommendations, which have greatly contributed to enhancing the clarity of our manuscript.

Responses to Comments of Reviewer #2 on NCOMMS-23-53106-T

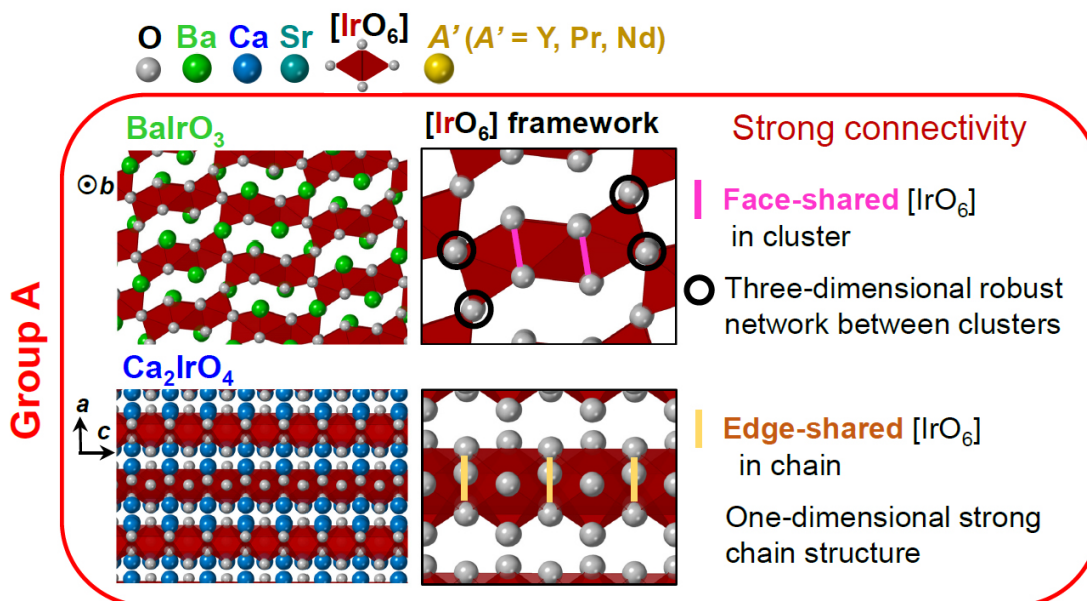
(General Comment) The authors present the synthesis and comprehensive characterization of barium iridates substituted with different (post-)transition metal elements as electrocatalysts for the oxygen evolution reaction (OER). They show that different substituents lead to different crystal structures with structural motifs of different inherent stability. Moreover, they show that the ionicity of Nb-O and Ta-O bonds strongly stabilized the materials, resulting in long-term stable catalytic performance. These results will be of high relevance for the future synthesis of catalysts that are stable under acidic conditions while reducing the amount of iridium atoms. I believe the work to be carried out with sufficient care and recommend reconsidering the manuscript after the authors have addressed the following comments.

(Re) The reviewer's comments on DOS calculation, impurities, XAS, and nomenclatures, reflecting his/her profound understanding of structural chemistry, DFT calculations, and electrocatalysis, were immensely valuable. We deeply appreciate all the impressive suggestions and meticulous feedback, which have greatly contributed to enhancing the clarity and strength of our revised manuscript. Below, we provide detailed responses to each comment.

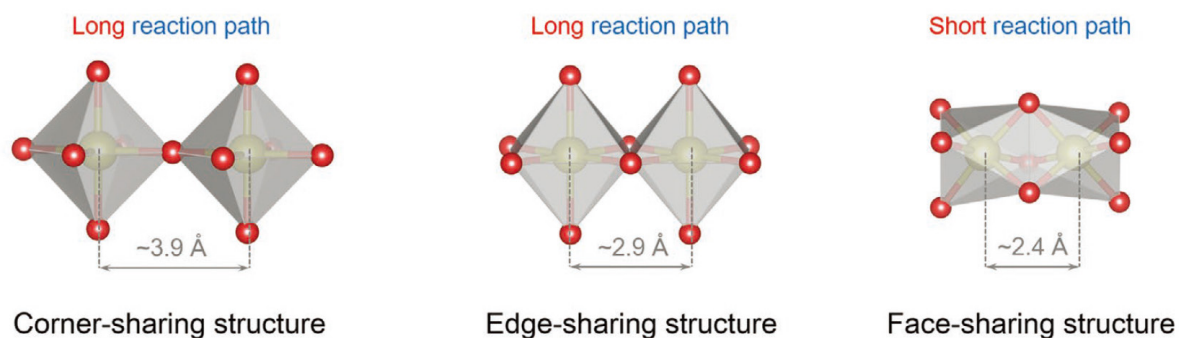
(Comment #1) The authors show a sketch in Fig. S22 that is supposed to show the stability of the bridging site in the trimer unless all three O are removed simultaneously. What is the justification for this stability? I believe that additional DFT calculations could help in unraveling the stability at the surface in conjunction with the experiments.

(Re) Oxygen redox has garnered significant attention over the last decade, as it can make a critical contribution to enhancing the capacity of cathode materials in Li-ion batteries and increasing the OER activity in oxide-type electrocatalysts. While many oxides exhibit high resistance to electrochemical corrosion under anodic conditions, structural instability can be induced by lattice oxygen oxidation, which is considered a major cause of degradation in many oxide catalysts (see, for example, Grimaud *et al.* "Activation of surface oxygen sites on an iridium-based model catalyst for the oxygen evolution reaction," *Nat. Energy* **2**, 16189 (2016); Schweinar *et al.* "Lattice oxygen exchange in rutile IrO₂ during the oxygen evolution reaction," *J. Phys. Chem. Lett.* **11**, 5008 (2020)). As depicted in our schematic illustration, this lattice oxygen oxidation ultimately leads to the gas-phase release of oxygen anions from the lattice. Therefore, the face-sharing configuration of oxygen octahedra offers a notable advantage in preventing the collapse of the oxygen-anion framework due to lattice oxygen activation.

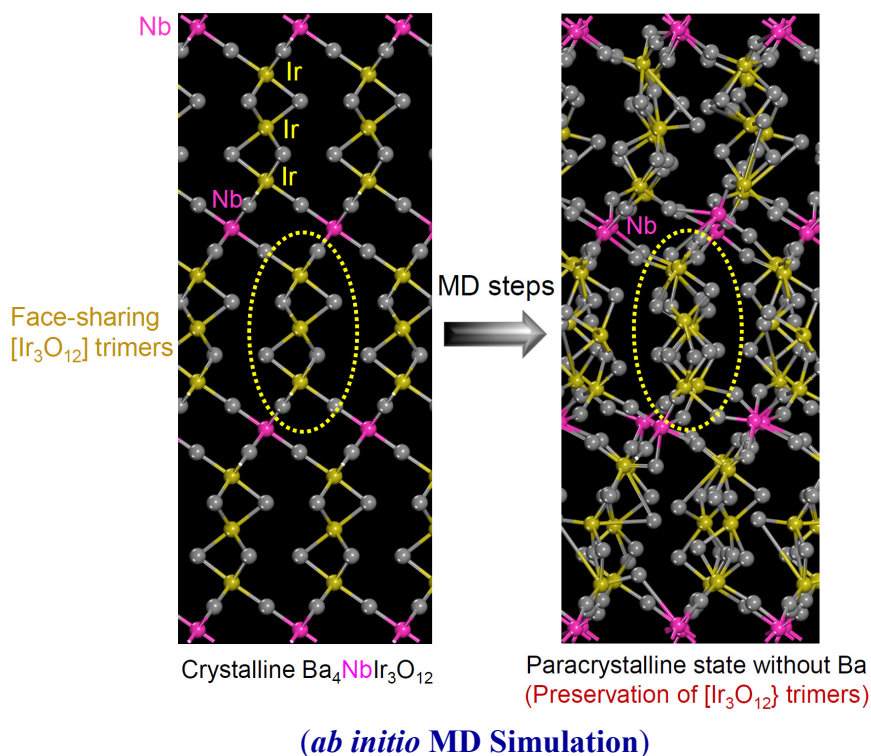
Two previous studies (Song *et al.*, *Energy Environ. Sci.* **13**, 4178 (2020); Guan *et al.*, *Adv. Mater.* **33**, 2103392 (2021)) have consistently demonstrated the correlation between the crystal structure and stability of oxide catalysts for the OER. In particular, Song *et al.* in 2020 ("Discovery of Crystal Structure–Stability Correlation in Iridates for Oxygen Evolution Electrocatalysis in Acid") reported that eleven high-activity $A_x\text{Ir}_y\text{O}_z$ -type complex iridates can be categorized into three distinct groups based on the degree of connectivity among the [IrO₆] octahedra. Furthermore, as illustrated below, iridates with strong edge-sharing or face-sharing connectivity exhibit substantial stability, showing no significant degradation of catalytic activity over many numbers of anodic cycling. This work thus underscores the importance of adopting a crystal-chemical perspective to assess the fundamental correlation between structure and stability in OER catalysts.



In 2021, Guan *et al.* ([“Exceptionally Robust Face-Sharing Motifs Enable Efficient and Durable Water Oxidation”](#)) also reported that 5H-polytype Ba₅Bi_{0.25}Co_{3.75}FeO₁₄, featuring face-sharing structures, exhibits significant OER activity and outstanding durability, surpassing those of the corner-sharing perovskite counterpart. Apart from its notable stability, Guan *et al.* claimed that the reduction in steric hindrance and the length of OER reaction path may accelerate OER kinetics. This acceleration is attributed to the shortened distance between B sites, transitioning from corner-sharing motifs (~3.9 Å) to edge-sharing structures (~2.9 Å), as described below. Therefore, it appears evident that the face-sharing [Ir₃O₁₂] trimers in BaIrO₃, as studied in our study, provide a robust structural framework.



Following the reviewer's suggestion for additional DFT calculations, we have conducted further *ab initio* molecular dynamics (MD) simulations to clarify the strong connectivity between the [Ir₃O₁₂] trimers in Nb-doped BaIrO₃. The simulations were performed using a supercell at an elevated temperature of 1200 K, without including Ba, to replicate Ba leaching conditions and expedite atom displacements. Despite significant deviation from the initial atomic positions, the organized structures of the [Ir₃O₁₂] trimers and Nb remain discernible, as depicted below. This outcome underscores the preservation of face-sharing octahedra, even in a paracrystalline state lacking long-range order. [We have incorporated these findings from the *ab initio* MD simulations into Supplementary Fig. 28 and have included a video clip as Supplementary Movie 1 in the revised version of our manuscript](#)



(Comment #2) Control experiments were performed with as-synthesized and ball-milled IrO_2 powders. How can it be excluded that the observed effects stem from impurities introduced during milling rather than the particle size as invoked by the authors?

(Re) Since we employed a typical solid-state synthesis method to prepare the seven iridates, a ball-milling process was a necessary step. We would like to note that we utilized a stabilized ZrO_2 jar and balls (see the photographs of the jar and balls below), as detailed in the Methods section of our original manuscript. ZrO_2 is known for its high hardness, typically ranking between 8 and 9 on the Mohs scale (with diamond ranking as 10). Therefore, we believe that ZrO_2 impurity contamination from the jar and balls is negligible. Given that the same milling process was used to obtain fine-particle IrO_2 , the distinct effect observed in Figure 6a does not appear to stem from impurities during the ball milling process.

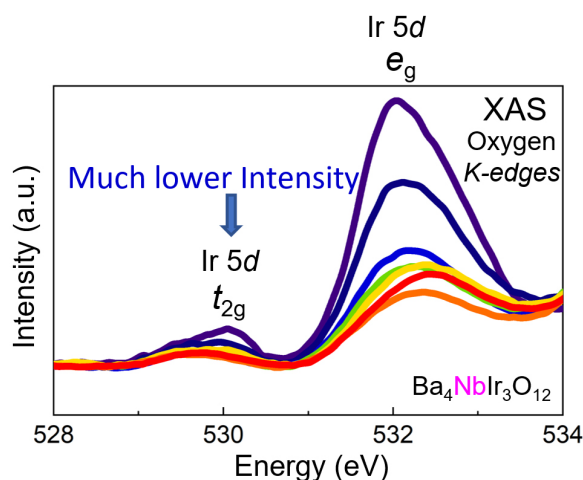


(Comment #3) In Fig. 5g, what is the origin behind the XAS peak intensity variations?

(Re) We would like to highlight that we utilized a soft X-ray source in total electron yield (TEY) mode for the O *K*-edge XAS analysis, focusing specially on the surface region of particles within a depth of <10 nm. As shown in Figures 4c and 4d, the surface crystalline structure transitions to an amorphous state as Ba dissolves into the electrolyte. When crystals transform into an amorphous phase, fundamental crystal symmetries, such as atom positions, bond lengths, and bonding angles, are significantly disrupted. Consequently, both the first peak (~530 eV), associated with the Ir 5d t_{2g} states, and the second peak (~532 eV), hybridized with the e_g states, should exhibit broadening due to the loss of symmetries, resulting in consistent reductions in their intensities.

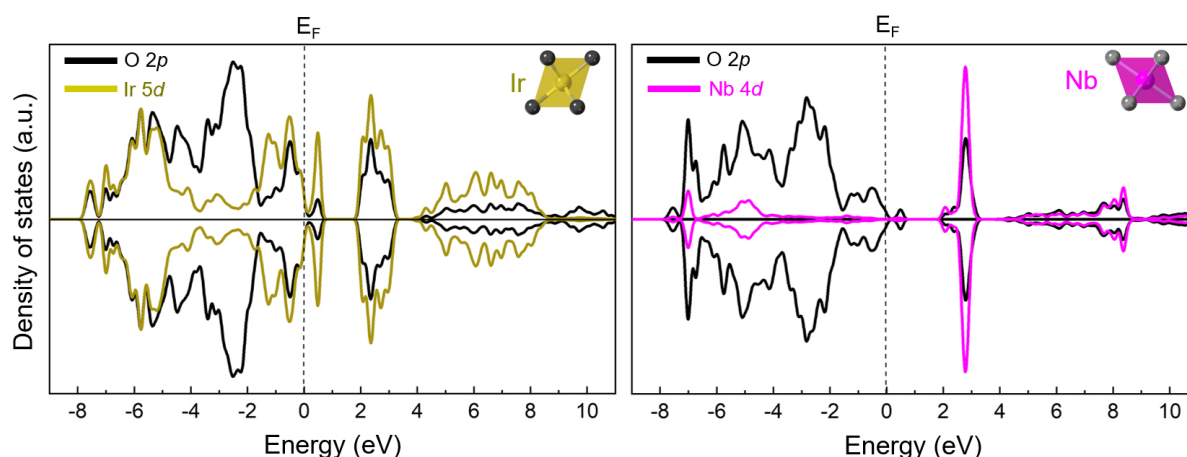
(Comment #4) How would DFT results change if spin configurations other than the low-spin were considered? Can the pDOS be reconciled with the experimental stability in all cases? Related to this, how was the magnetic order in the presence of Ir⁴⁺ treated? Calculations were spin-polarized but only one spin-channel is shown in the DOSs?

(Re) As pointed out by the reviewer, all the DFT calculations were carried out under the spin-polarized conditions. It is important to note that the selection of the low-spin state for Ir was NOT arbitrarily; rather it was based on experimental analysis of O *K*-edges in XAS. This analysis, well-documented in a previous study by de Groot *et al.* (“Oxygen 1s X-ray-absorption Edges of Transition-metal Oxides,” *Phys. Rev. B* **40**, 5715 (1989)), correlates the relative intensity of two peaks at 530–533 eV, corresponding to the hybridization with the t_{2g} and e_g states of transition metals, respectively, in the O *K* edge, directly with the spin state of the transition metals. Because the intensity reflects the empty DOS state that excited electrons can occupy, the *d* electron occupancy between the t_{2g} and e_g levels can be easily estimated from the O *K* edge. As shown in the following figure, our sample exhibits dominant intensity of the second peak, indicating largely occupied t_{2g} level and highly empty e_g level (corresponding to $t_{2g}^5 e_g^0$ electron configuration of low-spin Ir⁴⁺ with d^5). Therefore, the choice of low-spin state with ferromagnetic ordering in our DFT calculations appears to be in alignment with this XAS analysis. To provide further clarification, we have included additional explanations regarding the conditions of the DFT calculations in the Methods section.



Due to the majority of electrons being paired in the low-spin state ($t_{2g}^5 e_g^0$), the DOS plots of up-spin and down-spin electrons are very similar and symmetric to each other. As such, in our original manuscript, we only provided the total DOS. However, for clarification, we have now

included the spin-polarized DOS plots in Supplementary Fig. 27, as depicted below.



(Comment #5) I have some issues with the nomenclature adopted by the authors. Even though the term "hexagonal perovskite" can be found in the literature, "perovskite" refers to a crystal structure with corner-sharing octahedra. Calling everything that has ABO_3 stoichiometry a "something" perovskite is therefore highly misleading (let's leave aside that the solar-cell community is starting to call everything that absorbs light a perovskite).

(Re) We agree that the term 'perovskites' is misused in the solar-cell community. Meanwhile, the term 'hexagonal perovskites' has been commonly used in the field of solid-state chemistry to distinguish the face-sharing ABO_3 structure from the more familiar corner-sharing perovskite structure. A recent review article titled "[Hexagonal Perovskites as Quantum Materials](#)" (*Chem. Rev.* **121**, 2935 (2021)) by the Cava group at Princeton University thoroughly summarizes the key physical properties of various types of hexagonal perovskite oxides. Therefore, we do not find the use of the term 'hexagonal perovskites' in the field of oxides to be inappropriate or awkward.

(Comment #6) Another nomenclature issue is the use of "hybridization". This term refers to linear combinations of atomic orbitals on a given atom (i.e. sp^2 or sp^3 hybridization of carbon atoms). What the authors refer to on the other hand are linear combinations of atomic orbitals between atoms, which is covalence rather than hybridization.

(Re) It appears that the term 'orbital hybridization' has been utilized in a broader context, particularly concerning transition-metal oxides, to denote the overlapping states between the O 2p orbitals and the transition-metal d orbitals in DOS. This usage is well-documented in previous literature, such as in works by [Suntivich *et al.*](#) ("[Estimating Hybridization of Transition Metals and Oxygen States in Perovskites from O K-edge X-ray Absorption Spectroscopy](#)", *J. Phys. Chem. C* **118**, 1865 (2014)), [Frati *et al.*](#) ("[Oxygen K-edge X-ray Absorption Spectra](#)," *Chem. Rev.* **120**, 4056 (2020)), and [de Groot *et al.*](#) ("[Oxygen 1s X-ray-absorption Edges of Transition-metal Oxides](#)," *Phys. Rev. B* **40**, 5715 (1989)). In the realm of in transition-metal oxides, 'orbital hybridization' is commonly employed as an appropriate term.

(Comment #7) The terminology and language adopted by the authors do not make for easy reading. For example, "noncorrosive" refers to "corrosion resistant", "disconnection" to "bond

breaking”, “sustainability” to “long-term stability” or “molecular-level electron energy diagram” to “molecular orbital diagram”. Adopting conventional terms will make the manuscript significantly more accessible

(Re) We appreciate this comment Following the suggestion of the reviewer, we have replaced these somewhat awkward terms into other suitable and conventional ones for the benefit of our readers.

In the revised manuscript, all the additions in the text are highlighted in blue. New sets of results, along with additional content and the DOS plots in Figure 5f, have been included in Supplementary Figures 8, 9, 11, 21, 22, 27, 28, 29, 32, and 34, as well as Supplementary Movie 1. Furthermore, to emphasize the main claim of our work, we have also modified the title of the manuscript to “Effect of ionic-bonding d^0 cations on structural durability in barium iridates for oxygen evolution electrocatalysis”.

We would like to express our sincere gratitude for the reviewer’s valuable suggestions and recommendations. They have contributed to making our manuscript much clearer.

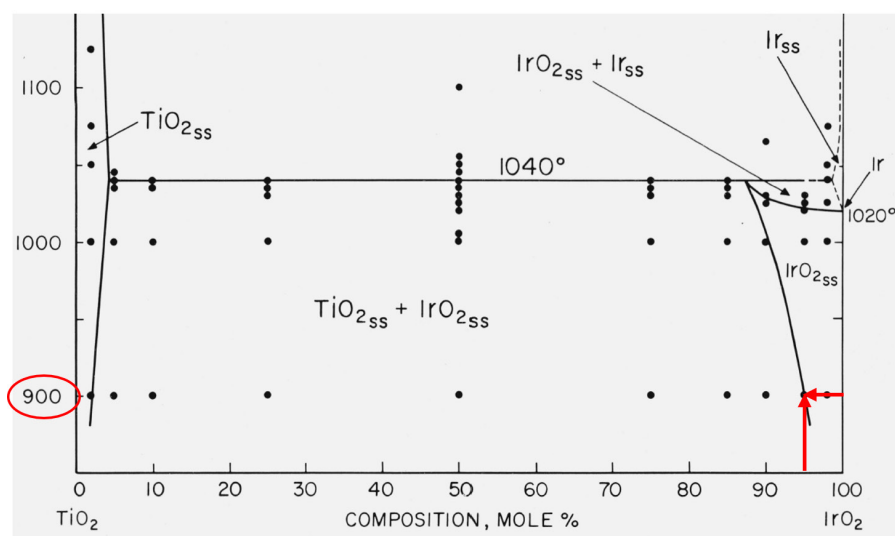
Responses to Comments of Reviewer #3 on NCOMMS-23-53106-T

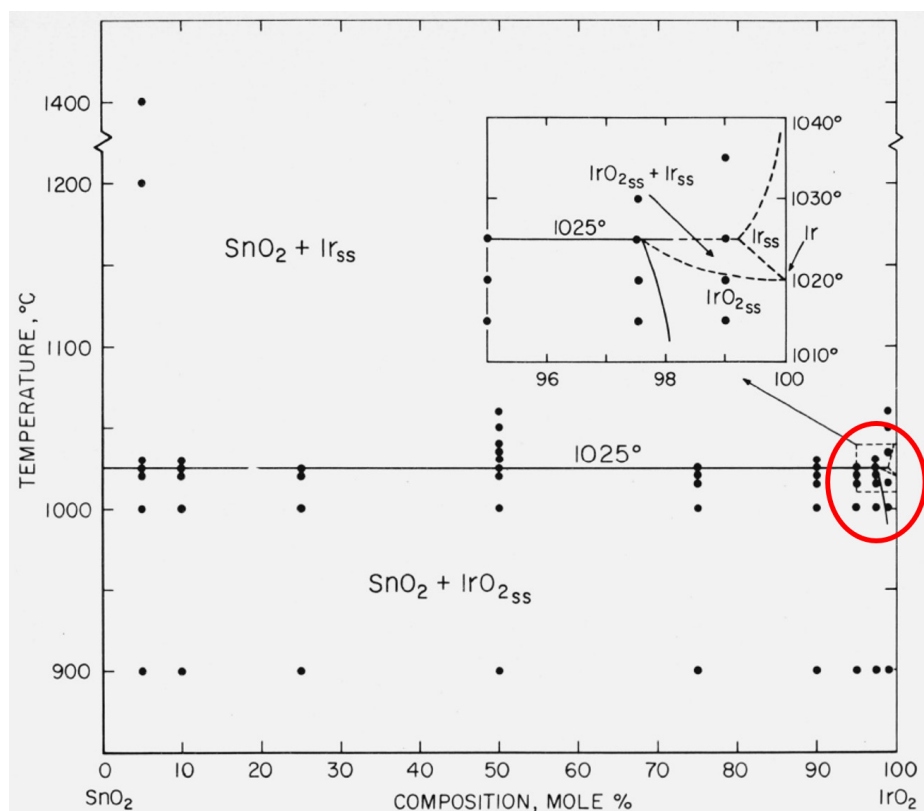
(General Comment) Sim et al. present a detailed study of Ir-based perovskites for the oxygen evolution reaction. Using advanced electron microscopy studies, SIMS and electrochemical measurements, they show how the structure of these materials changes as a result of the catalytic conditions. In the end, all reported materials turn into amorphous oxides at the surface (as is so often the case for Ir-based perovskites). For most materials, pure IrO_x is formed. In some cases, IrNbO_x or IrTaO_x is formed. The authors show that the extra Nb and Ta has a stabilizing effect compared to pure IrO_x , in agreement with previous research (e.g. pubs.acs.org/doi/10.1021/acsami.0c12609). Overall, I find that although the work is carefully performed and reported structural evolution is well-documented, the novelty of the conclusions is limited. It does not, as is claimed, provide any fundamentally new strategy for improving catalyst stability. Therefore, I do not recommend publication in Nature Communications. That said, using the detailed comments below, I do believe that the manuscript could be made suitable for a more specialized journal.

(Re) Based on in-depth knowledge regarding electrocatalysts, electronic structures of materials, and surface analyses, Reviewer #3 made helpful comments on the novelty of the work, the electronic states of amorphous phases, and further EDS analysis for clarification. We truly appreciate all the suggestions and meticulous comments to prepare the revised manuscript, which has been strengthened by more convincing and straightforward evidence for readers.

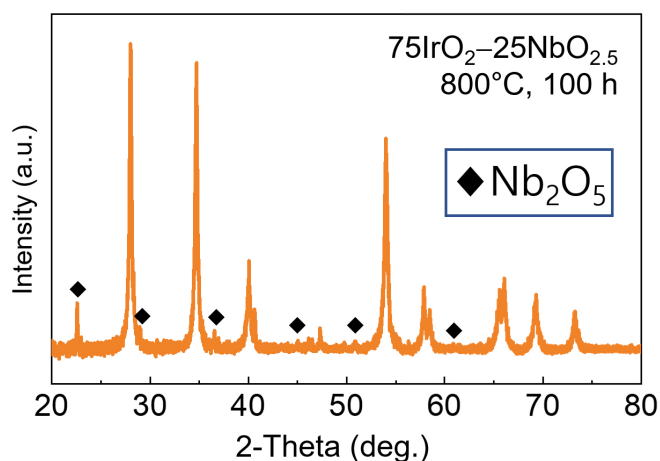
Before specifically addressing the eight comments made by the reviewer, we would like to clarify the novelty of our study. We are well aware of a previous publication mentioned by the reviewer regarding IrNbO_x (pubs.acs.org/doi/10.1021/acsami.0c12609, Spöri et al., *ACS Appl. Mater. Interfaces* **13**, 3748 (2021)). However, it is important to address the following facts to avoid misunderstandings.

(1) The most crucial point overlooked by the previous study by Spöri et al. is the significantly limited solubility of Nb in the rutile IrO_2 matrix. As indicated by the red arrows and ovals in the following phase diagrams of TiO_2 – IrO_2 and SnO_2 – IrO_2 , it should be noted that the solubility of insulating TiO_2 and SnO_2 into metallic IrO_2 is very low (less than 5% at 900°C) (McDaniel and Schneider, “Phase relations in the systems TiO_2 – IrO_2 and SnO_2 – IrO_2 in air,” *Journal of Research of the National Bureau of Standards – A. Physics and Chemistry* **71A**, 119 (1967)), despite the identical valence state of Ti^{4+} , Sn^{4+} , and Ir^{4+} and the identical rutile structure of TiO_2 , SnO_2 , and IrO_2 .





Moreover, because the crystal structure of Nb_2O_5 and the chemical bonding nature of Nb–O completely differ from the crystal structure of IrO_2 and the bonding characteristics of Ir–O, the solubility of Nb is extremely difficult to exceed 10% as well. To directly prove this considerably low solubility of Nb in rutile IrO_2 , we have carried out additional X-ray analysis using a powder mixture of 75IrO_2 – $25\text{NbO}_{2.5}$ annealed at 800°C for a sufficiently long period of time, 100 h, in air. As demonstrated below, the X-ray diffraction verifies the appearance of high-intensity Bragg reflections for the secondary Nb_2O_5 phase, **proving that the solubility of Nb in rutile IrO_2 is very low** (evidently less than 10% based on this diffraction pattern). Therefore, **the assumption of 40–60% solubility of Nb in the sample annealed merely at 300°C for 6 h in air and the subsequent discussion in the report by Spöri et al. are seriously misleading.** It is very likely that the sample shown in the study by Spöri et al. is a typical mixed-metal-oxide (MMO) composite rather than a solid solution.

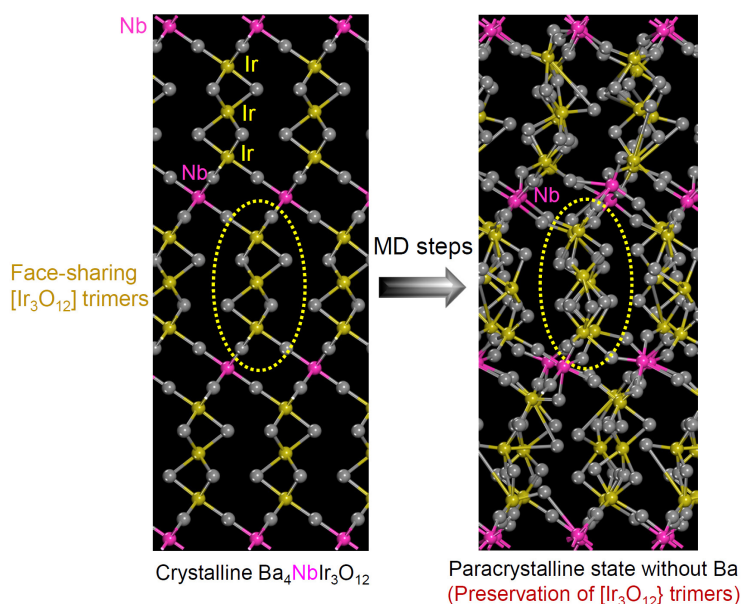


Supplementary Fig. 34

(2) It is noted that many mixed-metal-oxide (MMO) composites are commercially used as coating materials for DSA[®] (Dimensionally Stable Anodes), which are widely utilized devices with high conductivity and corrosion resistance as insoluble anodes in electrolysis (for example, visit '<https://jenningsanodes.com/dsa-electrodes/>'). To reduce the use of expensive Ir and simultaneously preserve the insolubility, electrochemically stable Ta and Nb oxides are typically added as composites. We wish to emphasize the novelty of our work, which achieves an unprecedentedly **high solubility of Nb and Ta** in Ir-based single-phase solid solutions and **elucidates the exact role of the dopants in the suppression of lattice oxygen activation**. This achievement should not be underestimated by merely comparing it to previous studies on MMO composites. Therefore, we have included the additional paragraph on page 8 in the revised manuscript in addition to providing the X-ray diffraction result of 75IrO₂–25NbO_{2.5} in Supplementary Fig. 34 to highlight the significant message regarding the solubility of Nb.

(Comment #1) The authors claim that Ir-based perovskites provide a platform for producing comparatively stable OER catalysts, because the IrO₆ octahedra are highly connected (more so than in e.g. rutile oxides). While I understand this argument, practice shows that it does not hold. In fact, the authors show that all perovskites amorphize at the surface. After this amorphization, it is unlikely that the edge-sharing octahedra structure is preserved. Hence, the claim seems unjustified. Instead, I think the data from the authors shows once more that the electronic structure of the materials is much more important than their crystal structure (Nb and Ta manage to stabilize the oxide, even when an amorphous layer is formed).

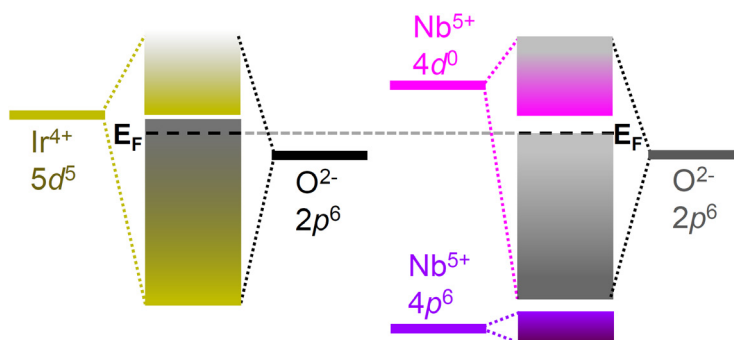
(Re) Yes, as precisely pointed out by the reviewer, we *definitely* agree that the different electronic structure between Ir–O and Nb–O is a key feature, and this is *exactly* one of the major claims of our study. An important point to note is that the amorphization in our samples was electrochemically induced by Ba leaching *at room temperature*. Consequently, the resulting phase is not of completely disordered random structure but specifically of a *paracrystalline* state maintaining short- and medium-range orders, although the original crystallographic symmetry and the subsequent long-range order disappear. To demonstrate the preservation the face-sharing high connectivity of [Ir₃O₁₂] trimers and the presence of Nb at the bridging sites between the trimers, we have carried out *ab initio* molecular dynamics (MD) simulation using a supercell without Ba.



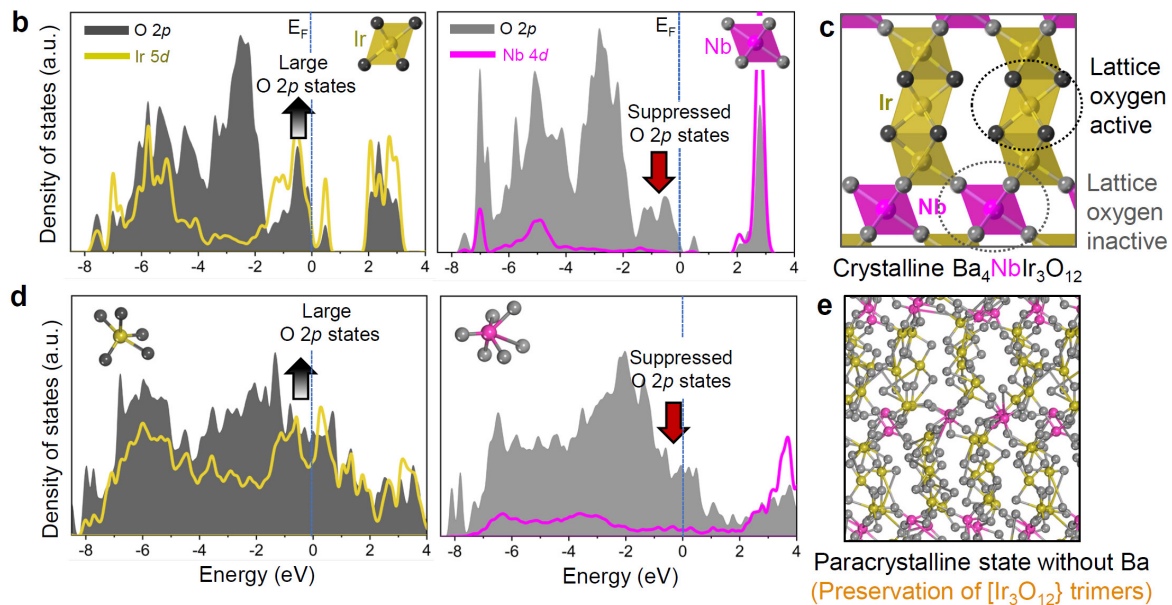
Moreover, this MD simulation has been performed at an elevated temperature, 1200 K, to accelerate the atom position perturbation. As readily recognized above, the overall configuration of the $[\text{Ir}_3\text{O}_{12}]$ trimers and the bridging Nb in the supercell remains clearly identified, despite the loss of the original symmetry is lost. Therefore, it is noted that the face-sharing $[\text{Ir}_3\text{O}_{12}]$ trimers are structurally robust. We have included theses *ab initio* MD simulation results in Supplementary Fig. 28 and provided a video clip as Supplementary Movie 1 in our revised version of the manuscript to confirm the *paracrystalline* state after Ba leaching. As will be clarified in the response to Comment #2 below, we can thus verify that the role of Nb, which suppresses the lattice oxygen activation, does not vary in this paracrystalline phase after Ba leaching.

(Comment #2) Much of the analysis and arguments are based on the bulk structure of the perovskite. However, as discussed in the previous point, this is not useful when the electrode surface becomes amorphized. From this perspective, the lengthy TEM analysis of the bulk crystal structure could be moved to the SI in large part. Also, the DFT analysis in Fig. 5 becomes **meaningless**, because it assumed the bulk perovskite structure. It is not directly obvious that the Nb would have the same effect in amorphous IrNbO_x formed once the Ba has left.

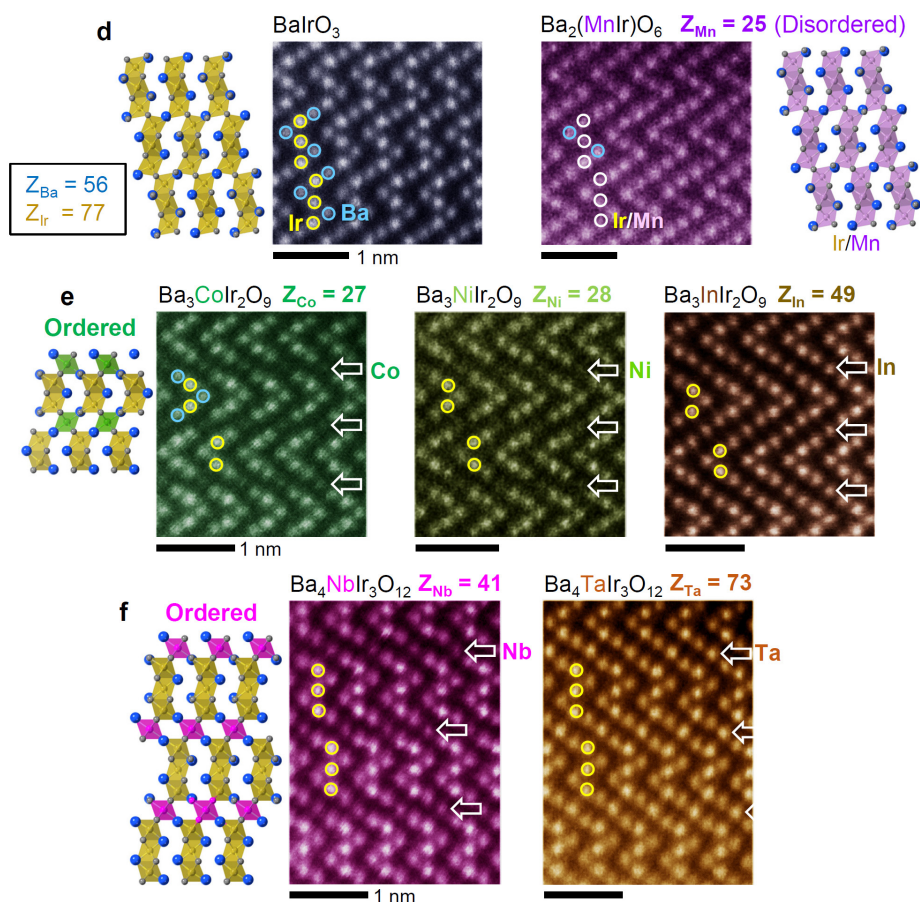
(Re) We acknowledge that this comment raises a significant point regarding the suitability of DOS plots for a crystalline phase. As demonstrated by the *ab initio* MD simulations above, the $[\text{Ir}_3\text{O}_{12}]$ trimers and the bridging Nb are preserved in the amorphous state induced by electrochemical Ba leaching, even though the original long-range order and symmetry are no longer maintained. Therefore, we assert that describing the surface of our iridate samples as “paracrystalline” is a more precise characterization. In addition, the electronic configuration of Nb^{5+} with completely empty $4d$ states remains unchanged regardless of whether the solid phase is crystalline or amorphous. As a result, the following schematic description of the ionic bonding characteristics with neighboring oxygens is applicable to explain the role of Nb in paracrystalline or amorphous phases. In this context, **we do NOT believe that our DOS results in Figure 5 are meaningless.** Despite being acquired from a crystalline supercell, they serve as a crucial basis for explaining the significant feature of Nb and Ta in suppressing lattice oxygen participation.



To further clarify the consistent effect of Nb on the reduction of lattice oxygen contribution in the paracrystalline state, we have carried out additional DFT calculations using a paracrystalline supercell prepared by the *ab initio* MD simulation. As anticipated, the relatively lower DOS of O $2p$ near the Fermi level in Nb–O can be verified, indicating that role of Nb remains unaffected by whether the sample is crystalline or amorphous. We have added this new set of DOS results in Figures 5f and 5g in the revised manuscript, as shown below.



We strongly believe that clearly demonstrating the initial crystal structure and chemical ordering in Ba-based iridates is necessary, as the paracrystalline state after Ba leaching is not independent of the original crystal structure consisting of face-sharing $[\text{Ir}_3\text{O}_{12}]$ trimers in Nb and Ta-doped samples. In response to the reviewer's suggestion, we have removed the simulated images in Figure 2 and instead included them in Supplementary Fig. 9 in the revised version, as shown below.

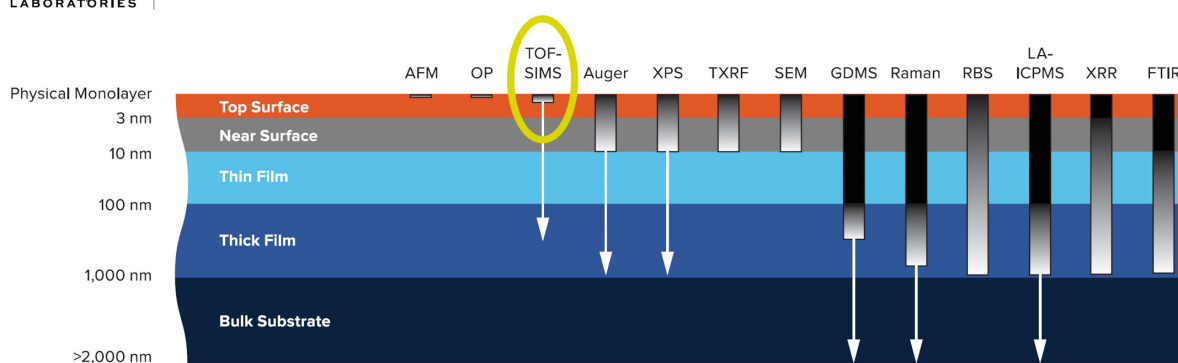


(**Comment #3**) It would be good if the authors are a bit more specific in their description of the SIMS measurements. The SIMS method employed here to quantify the degree of lattice oxidation is not strictly measuring this quantity. **What it measures is the depth in the sample to which lattice oxidation occurs.** It does not provide a ratio between lattice oxygen evolution and the “regular” adsorbate evolution mechanism. It is important that the authors make this distinction for clarity.

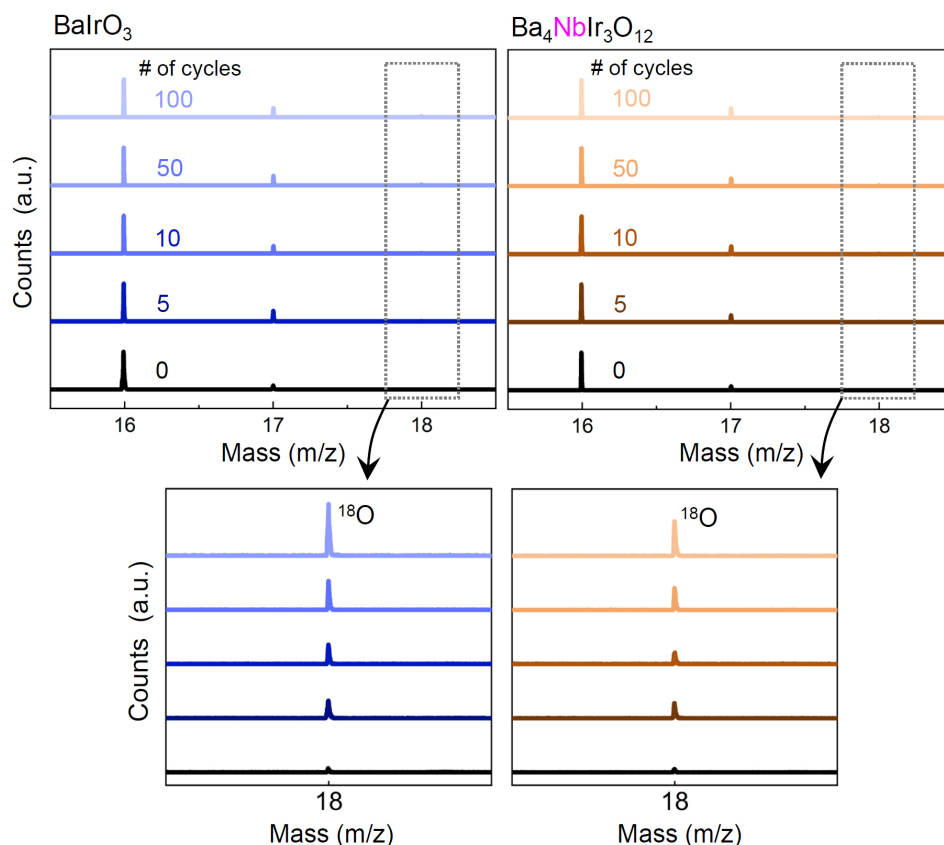
(**Re**) We would like to clarify that **secondary ion mass spectrometry (SIMS) is NOT a tool for measuring the depth of an active surface layer.** SIMS is a well-known surface analysis technique that provides the quantitative compositional information of elements. Specifically, because SIMS is based on mass spectrometry, it is widely utilized to detect isotope elements. We emphasize that distinguishing isotope ^{18}O from normal ^{16}O in the surface region is a major task in our study. Therefore, the use of time-of-flight (TOF) SIMS is of great significance for precisely examining the relative concentration of ^{18}O at the surface among the samples. As illustrated in the renowned EAG chart below, the depth resolution of TOF-SIMS is 1–2 nm. Consequently, the relative concentration of isotope ^{18}O with respect to that of normal ^{16}O at the surface within a depth of 1–2 nm can be efficiently measured by SIMS.



Typical Analysis Depths for Techniques

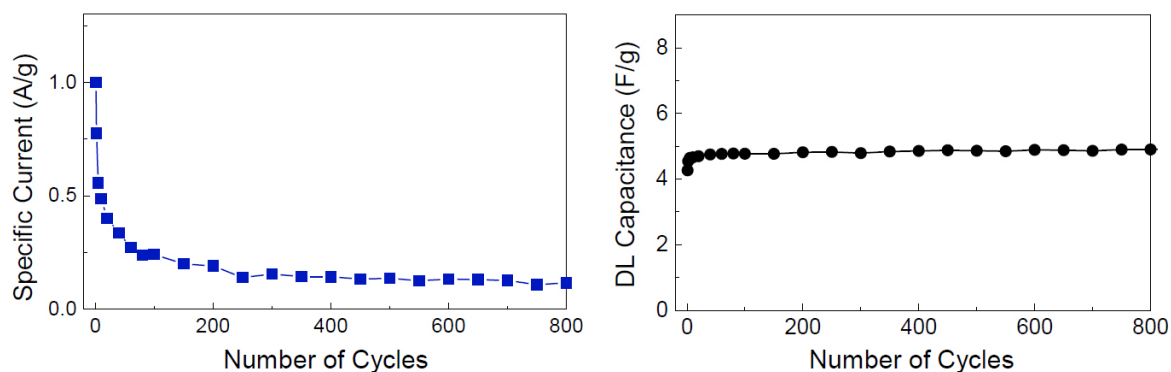


It is also worth noting that there is currently no available analytical method that can precisely quantify the ratio between the lattice oxygen contribution and the regular adsorbate contribution, while many researchers of OER catalysts are eager to develop such methods. In this regard, SIMS analysis is one of the suitable tools that can directly indicate the relative degree of the lattice oxygen contribution among samples. To facilitate precise comparisons and demonstrate the substantial reduction of the ^{18}O signal in $\text{Ba}_4\text{NbIr}_3\text{O}_{12}$, we have included mass spectra in a range of $m = 16\text{--}18$ of BaIrO_3 and $\text{Ba}_4\text{NbIr}_3\text{O}_{12}$ cycled in an electrolyte containing H_2^{18}O in Supplementary Fig. 29 in the revised manuscript, as shown below.



(Comment #4) The degradation of the pure IrO_2 samples reported by the authors is much too fast to be related to dissolution of IrO_2 . It seems likely that particle detachment plays an important role here, which is mostly due to the method for depositing the catalyst particles rather than their intrinsic properties.

(Re) As provided below, our DL capacitance measurement of the IrO_2 sample shows that the capacitance value remains nearly unchanged with anodic cycling. This directly indicates that the intrinsic catalytic activity of IrO_2 decays at an initial stage of cycling (~ 200 cycles) rather than detachment of particles from the electrode. An intriguing feature is that further serious degradation is no longer observed after 200 cycles.



In fact, we have been working on this degradation behavior and found that it is *not* exclusively observed in IrO_2 *but* rather frequently identified in other oxide-based catalysts. Our preliminary analysis results imply that this behavior is associated with unit-cell-scale amorphization (or

paracrystallization) at the catalyst surface. Once the loss of crystallinity by symmetry breaking occurs at the surface, it appears that the intrinsic catalytic property significantly can diminish. We believe that there will be an opportunity to report this degradation behavior as an independent study.

(Comment #5) Fig. 1: Ir and O are both labelled grey in the crystal structures. This makes it them very difficult to interpret.

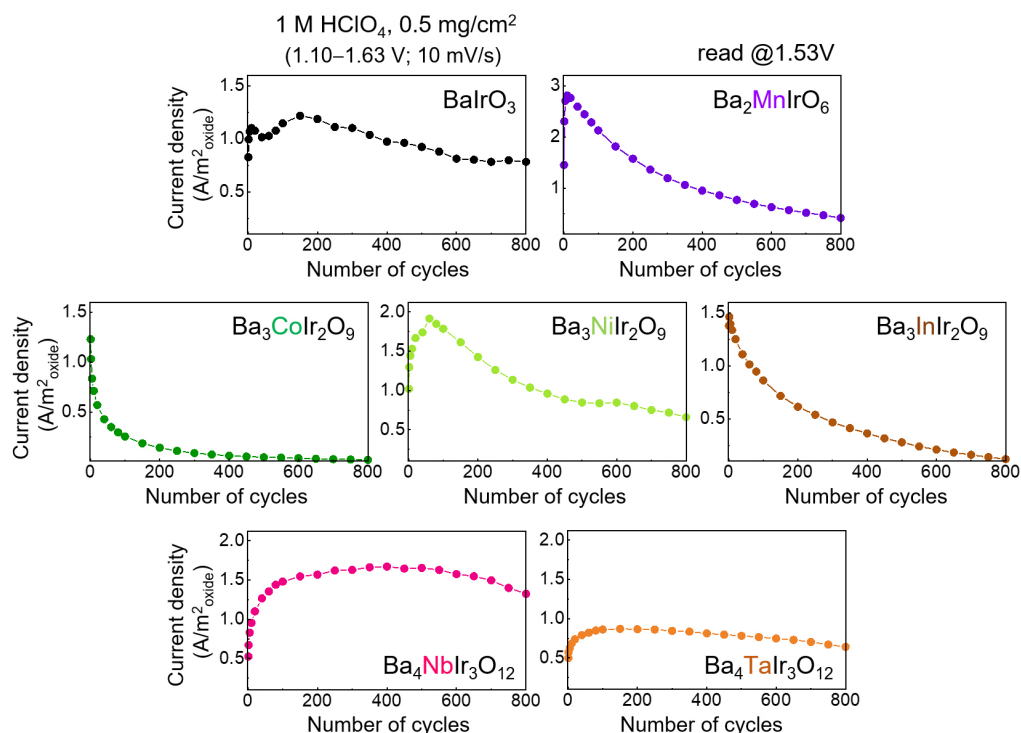
(Re) We appreciate this observant comment. We have modified each label with a different color in Figure 1 for readers in our revised manuscript.

(Comment #6) Fig. 3: It is not clear to me how the current density is defined here. At what potential is the OER activity measured? How is the capacitance used for the normalization defined? I think it is important that the authors note that such a normalization by capacitance does not necessarily yield a fair comparison of current densities between the materials, because the capacitance per unit surface area likely differs for the different materials. And can the authors exclude the possibility of degradation due to particle detachment during OER (which is not an intrinsic material property, but rather a function of how the catalyst was deposited on the substrate)?

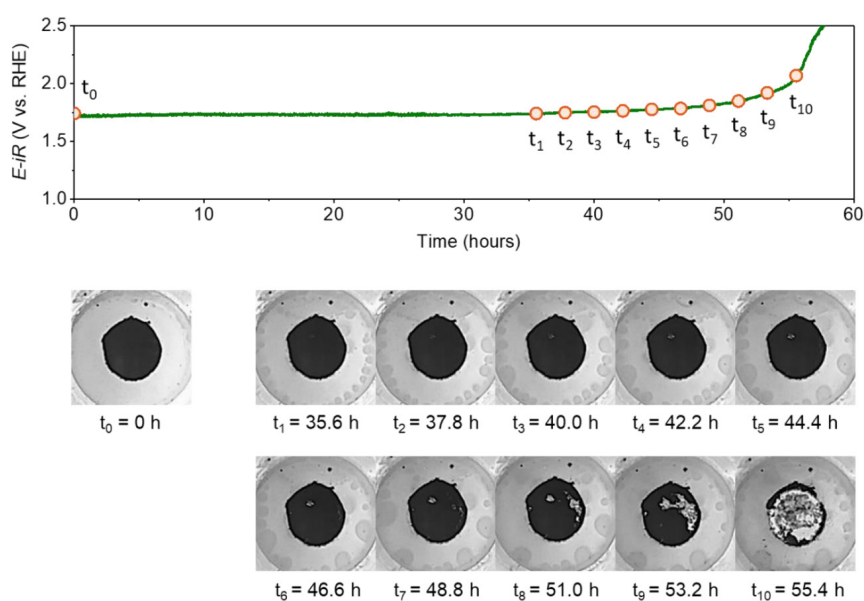
(Re) As reported in previous studied by the Jaramillo group in 2013 and 2016 (McCroy *et al.*, *J. Am. Chem. Soc.* **135**, 16977 (2013); Jung *et al.*, *J. Mater. Chem. A* **4**, 3068 (2016)), the double-layer (DL) capacitance is generally used to estimate the electrochemically active surface area (ECSA). Because this DL capacitance is measured in a non-faradaic potential range, it strongly correlates with the BET surface area (Jung *et al.*, *J. Mater. Chem. A* **4**, 3068 (2016)), and has thus been widely utilized as a parameter to obtain the ECSA and thereby benchmark a variety of oxide catalysts for OER activity per unit area since the initial suggestion in 2013 (McCroy *et al.*, *J. Am. Chem. Soc.* **135**, 16977 (2013)). The ECSA is acquired from the following equation:

$$\text{ECSA} = C_{\text{DL}}/C_s$$

where C_{DL} is the measured DL capacitance of a catalyst material and C_s is the specific capacitance of the sample per unit area under a certain identical electrolyte condition. Specific capacitance has been measured for various metal electrodes in acidic and alkaline solutions, with typical values ranging between $C_s = 0.015\text{--}0.110\text{ mF/cm}^2$ in acidic H_2SO_4 . In the study of McCroy *et al.* (*J. Am. Chem. Soc.* **135**, 16977 (2013)), a general specific capacitance value of $C_s = 0.035\text{ mF/cm}^2$ in an acidic condition was used as a reasonable approximation. Therefore, we have adopted this value for our specific capacitance ($C_s = 0.035\text{ mF/cm}^2$) to estimate the ECSA of each sample. To avoid any misunderstanding, we have revised our data in Figure 3 based on the ECSA suggested by McCroy *et al.*, as shown below, and have provided additional details regarding the ECSA in the Methods section in our revised manuscript for readers.



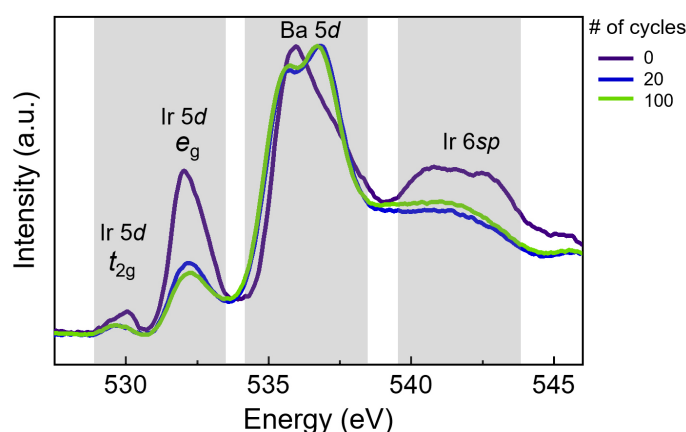
As demonstrated by the cycling results above, the Nb- and Ta-doped samples show no significant reduction in the OER current density. Therefore, the detachment of particles can be regarded as negligible in these cases. Conversely, as shown in the EDS maps, Mn, Co, Ni, and In undergo serious dissolution into the electrolyte, leading to lattice decomposition and simultaneous particle detachment from the rotating disk electrode (RDE), which are mutually coupled processes. A recent report by Li *et al.* (*Nature Catalysis* **5**, 109 (2022)) also demonstrated significant particle detachment even in thin-film-type Co₂MnO₄ catalysts firmly deposited on a stable substrate during a chronopotentiometric stability test, as shown below. Therefore, we anticipate that the OER current density would diminish more rapidly as the catalyst becomes more unstable, accompanied by particle detachment from the electrode.



Li *et al.* *Nature Catalysis* **5**, 109 (2022)

(Comment #7) The labeling of the O K-edge spectra is a bit oversimplified. Since Ir is not the only metal in the material, it is not certain that the resonances in the O K-edge between 528 and 533 eV can be attributed to Ir-O hybridized empty states. In fact, most metal oxides show resonances in this range. Hence, Ba-O and Nb-O resonances will likely be present here as well.

(Re) A recent review article by Frati *et al.* (“Oxygen K-edge X-ray Absorption Spectra,” *Chem. Rev.* **120**, 4056 (2020)) summarized very well the key features of O K edges in X-ray absorption spectroscopy (XAS) across various oxide materials. The O K edges of ABO_x-type perovskite oxides typically consist of three major peaks: The first peak (528–534 eV) corresponds to the excitation from the O 1s state to the hybridized O 2p–B *d* state, while the second (535–540 eV) and third peaks (>540 eV) are attributed to the excitations of O 1s to O 2p–A *d*, and O 2p–B *sp*, respectively. We observed similar O K edges of Nb-doped BaIrO₃. The following figure shows the full K edge. As pointed out by the reviewer, the middle peak represents the hybridized O 2p–Ba 5*d* state. Notably, Nb constitutes 25% of the B-site cation in Nb-doped BaIrO₃ and the Nb 4*d* states do not significantly overlap with O 2*p* in the DOS. Consequently, the first pair of peaks in the range of 528–534 eV largely originates from the hybridized O 2*p*–Ir 5*d* state. We thus focused on these peaks in our original manuscript. To provide the entire O K edges and ensure that the labeling is not oversimplified, we have included the following figure in Supplementary Fig. 32 in our revised manuscript.



(Comment #8) SI Figure 23: O¹⁸ increases instead of decreasing (which the caption says it should do). Was something mislabeled?

(Re) The TOF SIMS result presented in the Supplementary Information indicates that Ta has an identical effect on suppressing lattice oxygen oxidation. Consequently, a smaller amount of ¹⁸O is detected in Ba₄TaIr₃O₁₂ compared to pristine BaIrO₃. This serves as further consistent evidence supporting the role of ionic-bonding *d*⁰ cations (Ta⁵⁺) in suppressing lattice oxygen contribution.

All the additions and corrections in the text have been highlighted in blue in the revised manuscript. New sets of analysis results, along with further additions and DOS plots, have been included in Figure 5f, Supplementary Figures 8, 9, 11, 21, 22, 27, 28, 29, 32, and 34, as well as Supplementary Movie 1. In addition, we have changed the title of this manuscript into “Effect of ionic-bonding *d*⁰ cations on structural durability in barium iridates for oxygen evolution electrocatalysis” to specify the main claim of our work.

The observant and meticulous comments and suggestions of the reviewer make us realize that he/she is one of the authorities working on both electrocatalysis and energy materials for a long period of time. We offer our *sincere* and *special* gratitude for the invaluable comments of the reviewer. They have made our manuscript much clearer and stronger.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

In my opinion, the authors have addressed satisfactorily my remarks and the manuscript has been considerably improved.

However, I do have a minor comment. Regarding the response to comment 5, it appears that ECSA has been measured using carbon-containing ink. If this is indeed the case, the ECSA values obtained could be rendered meaningless, as the area of the carbon material utilized for analysis might greatly exceed that of the material being studied.

Reviewer #2 (Remarks to the Author):

The authors have made an effort to address my previous comments as well as those of the other reviewers. While the additional data and changes in the manuscript address some of these comments, other points remain to be clarified.

1) The added ab initio MD trajectory is an extreme case in terms of temperature and Ba content, which raises questions about its representability for the actual experimental samples. In particular, it is unclear how omitting all Ba²⁺ changes the oxidation state of the Ir and Nb transition metals and hence the stability and reactivity. Also, while the circled area indeed remains fairly intact throughout the simulated time, the surrounding trimers are severely distorted. Is this due to the temperature or the change in oxidation state? Is it still correct to state that the trimers are structurally stable?

2) I don't see how the DOS in Fig. S27 can be for Ir $t_{2g}^5 e_g^0$ in a ferromagnetic order as stated by the authors. In this case, I would expect the singly occupied t_{2g} to lead to more marked asymmetries in the DOS (which looks completely AFM).

Reviewer #3 (Remarks to the Author):

Sim et al. have provided a significant amount of new data in their revised manuscript. Using this data and discussion of the literature, they clarified the novelty of their manuscript very well in the rebuttal. The transfer of these arguments into the manuscript could still be improved (see below). However, assuming proper treatment of these comments I feel that the authors have brought the manuscript to a level that is suitable for Nature Communications. No further review required from my side.

1) The partial preservation of order in the Ba-leached BaIrNbO_x material is a very interesting point, that has strong implications for the usefulness of employing (unstable) precursor materials such as perovskites to create stable “activated” catalysts. It shows that the nature of the precursor really matters, not only for the openness of the morphology of the ensuing IrO_x catalysts (which seemed to be the case in most previous studies with perovskite or IrNi precursors), but also for the crystal structure. I feel that the authors should highlight this more in the text, e.g. in abstract and/or introduction

2) As I mentioned before, the stabilizing effect of Nb and Ta in IrO_x has been previously established. In

their rebuttal, the authors clearly discuss the difference between their work and what was done before. If feel that this discussion was not very clear in the manuscript, however.

3) The capacitance measurements in supplementary figure 24 actually address my concern regarding the possibility of particle detachment as one of the reasons for degradation. One can clearly

Response to Comment of Reviewer #1 on NCOMMS-23-53106A

(Comment) In my opinion, the authors have addressed satisfactorily my remarks and the manuscript has been considerably improved. However, I do have a minor comment. Regarding the response to comment 5, it appears that ECSA has been measured using carbon-containing ink. If this is indeed the case, the ECSA values obtained could be rendered meaningless, as the area of the carbon material utilized for analysis might greatly exceed that of the material being studied.

(Re) We gratefully acknowledge this comment on the effect of acetylene black on the ECSA. As the mass ratios were adjusted to be 10:1 for the catalyst to acetylene black, we identified that the contribution of added acetylene black and Nafion binders was 5–20% of the total DL capacitance through directly measuring their DL capacitance without catalyst particles. To precisely represent the OER current density per unit area, which had been underestimated, in addition to the DL capacitance, we have made modifications on all the data in Figure 3 and Supplementary Figure 24 in the revised manuscript.

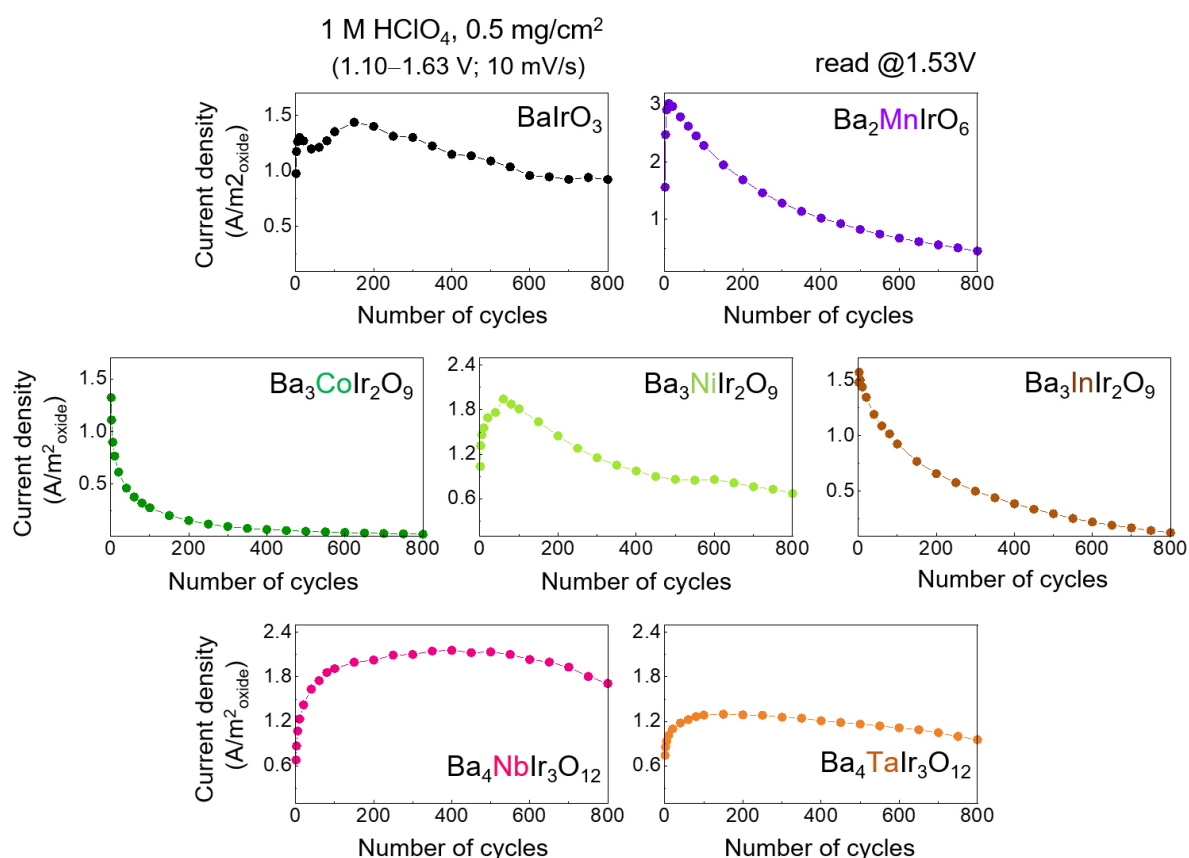
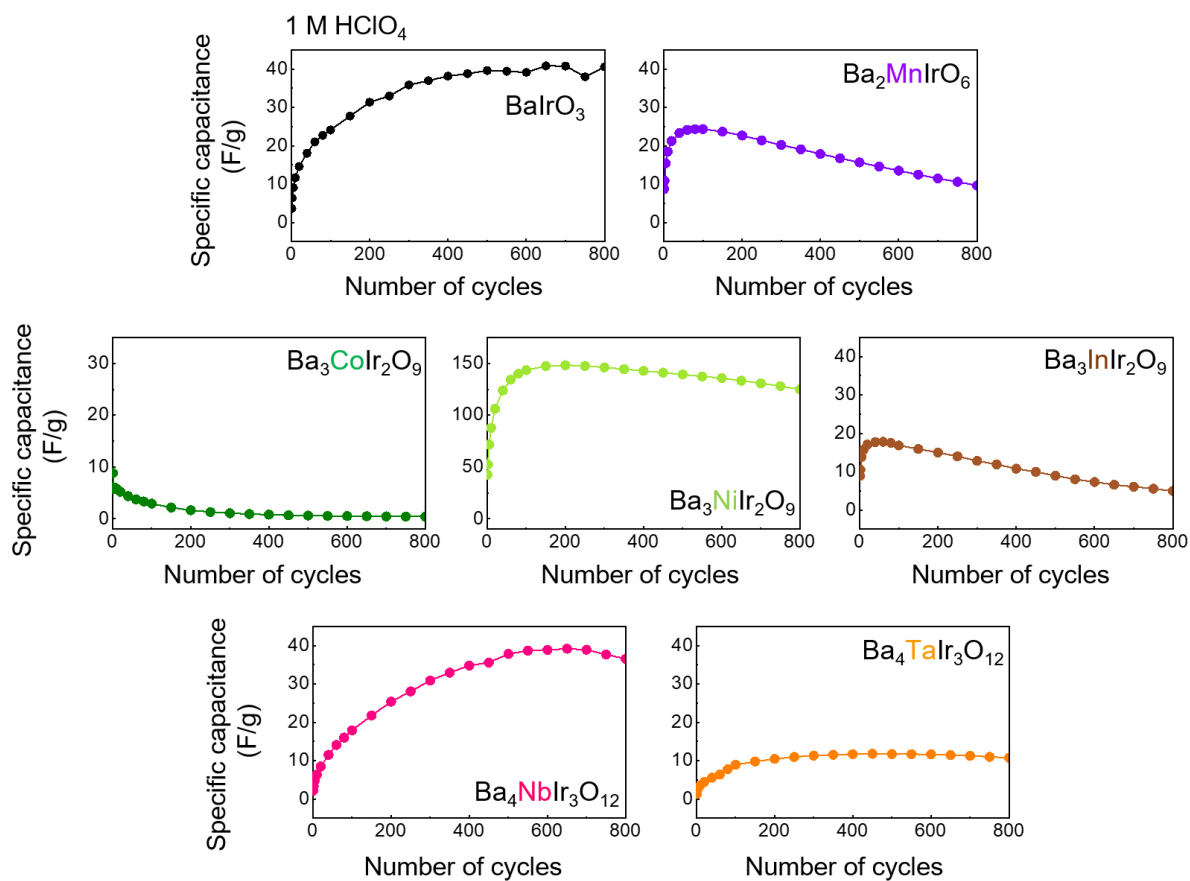


Figure 3



Supplementary Fig. 24.

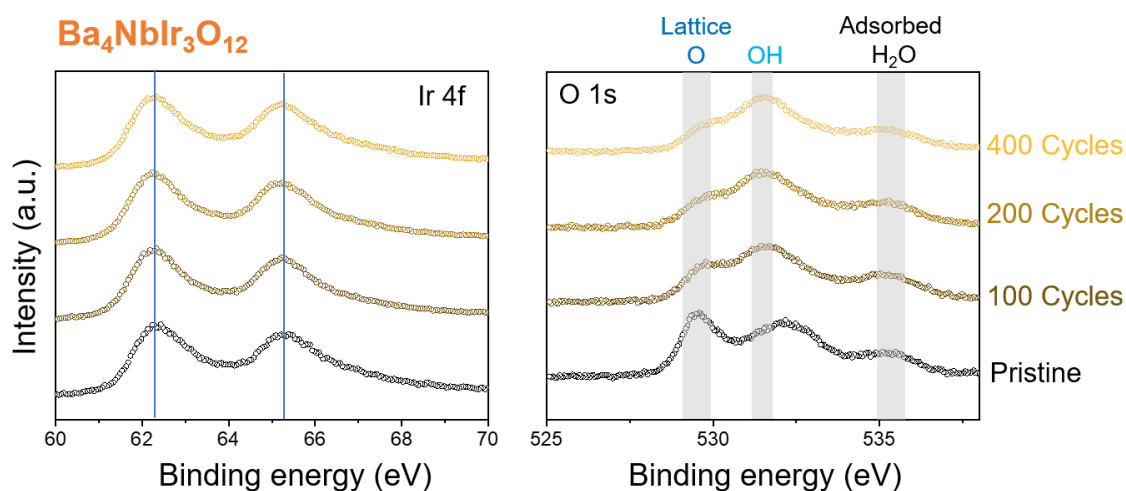
Responses to Comments of Reviewer #2 on NCOMMS-23-53106A

(General Comment) The authors have made an effort to address my previous comments as well as those of the other reviewers. While the additional data and changes in the manuscript address some of these comments, other points remain to be clarified.

(Comment #1) The added *ab initio* MD trajectory is an extreme case in terms of temperature and Ba content, which raises questions about its representability for the actual experimental samples. In particular, it is unclear how omitting all Ba^{2+} changes the oxidation state of the Ir and Nb transition metals and hence the stability and reactivity. Also, while the circled area indeed remains fairly intact throughout the simulated time, the surrounding trimers are severely distorted. Is this due to the temperature or the change in oxidation state? Is it still correct to state that the trimers are structurally stable?

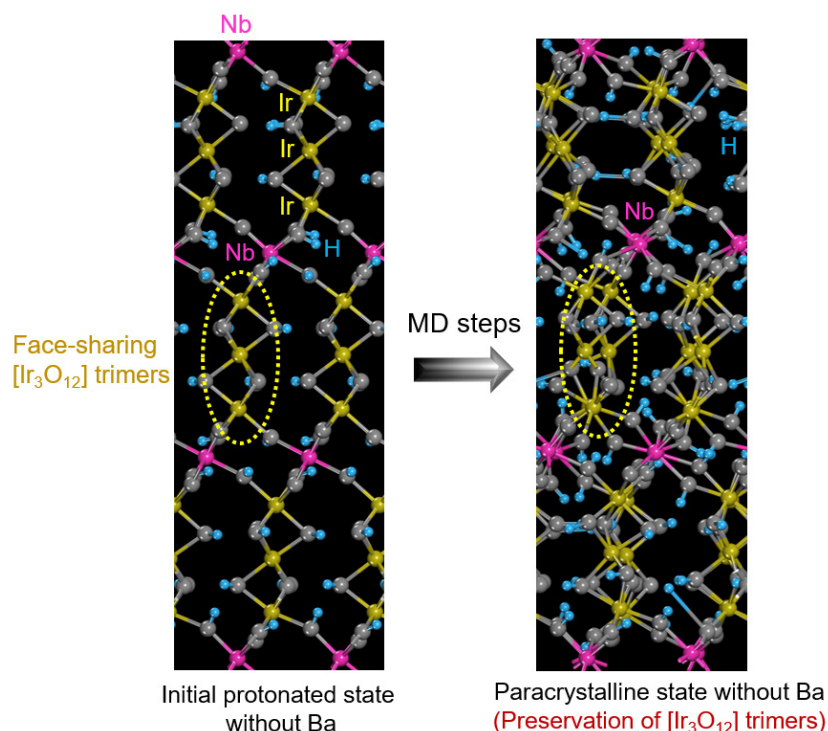
(Re) The MD simulation was performed at an elevated temperature (1200 K) to facilitate atom displacement. Despite this high-temperature condition, it is noted that the basic $[\text{Ir}_3\text{O}_{12}]$ -trimer framework does not break down.

To construct a more realistic supercell in response to the reviewer's comments, we first carried out additional XPS analyses. As shown below, the position of the Ir 4f peaks does not vary with anodic cycling, indicating that the valence state of Ir hardly changes. In contrast, the O 1s peak for OH becomes dominant, while the peak for lattice O diminishes. This directly demonstrates that the charge neutrality without Ba is achieved through protonation from the electrolyte, resulting in the formation of oxyhydroxide.

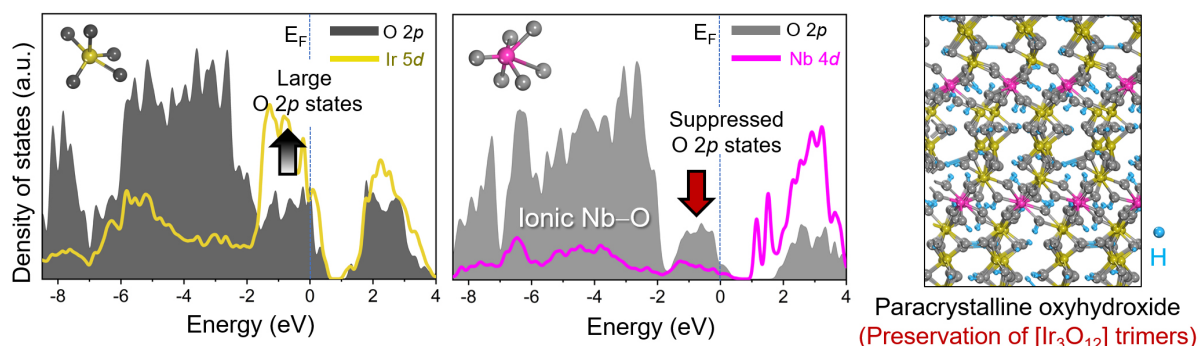


Supplementary Fig. 24a

We have conducted *ab initio* MD simulations at 300 K to acquire a Ba-free paracrystalline supercell with charge neutrality. It is consistently observed that face-sharing connectivity in each $[\text{Ir}_3\text{O}_{12}]$ trimer is preserved even in this paracrystalline state lacking long-range order. We have finally obtained the DOS plots of $[\text{IrO}_6]$ and $[\text{NbO}_6]$ octahedra from this supercell and verified that the O $2p$ states near the Fermi level in the $[\text{NbO}_6]$ octahedra are substantially suppressed. It appears that our key message regarding the effect of d^0 Nb and Ta dopants on the suppression of lattice oxygen activation is consistently supported irrespective of whether the supercell is a crystalline oxide or a paracrystalline oxyhydroxide. We have included the following figures in Figures 5f and 5g and Supplementary Fig. 24b in the revised manuscript.



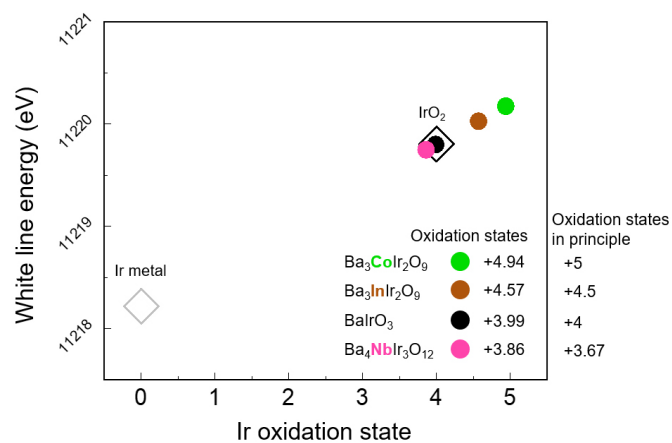
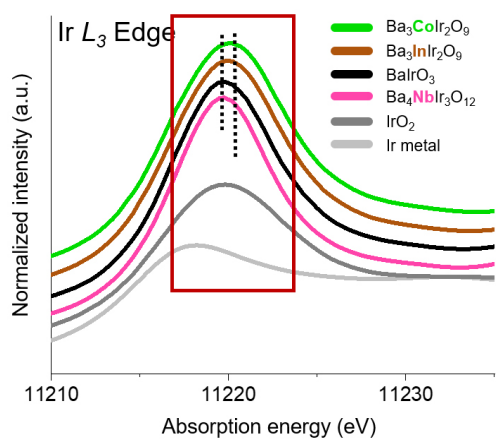
Supplementary Fig. 24b (*ab initio* MD Simulation)



Figures 5f and 5g

(Comment #2) I don't see how the DOS in Fig. S27 can be for $\text{Ir } t_{2g}^5 e_g^0$ in a ferromagnetic order as stated by the authors. In this case, I would expect the singly occupied t_{2g} to lead to more marked asymmetries in the DOS (which looks completely AFM).

(Re) We appreciate this observant comment. As Nb^{5+} is doped in this case, one-third of the Ir atoms are $\text{Ir}^{3+}(t_{2g}^6 e_g^0)$ rather than Ir^{4+} for charge neutrality. As shown in Supplementary Fig. 8 in our manuscript (see the following figure), the overall valence state from the XANES analysis of the Ir L_3 edge was indeed found to be +3.86. Consequently, the influence of unpaired t_{2g} electrons is significantly reduced, resulting in a nearly symmetric feature in the DOS of $\text{Ba}_4\text{NbIr}_3\text{O}_{12}$, even though the AFM order was not assigned to Ir during the calculation.



Responses to Comments of Reviewer #3 on NCOMMS-23-53106A

(General Comment) Sim et al. have provided a significant amount of new data in their revised manuscript. Using this data and discussion of the literature, they clarified the novelty of their manuscript very well in the rebuttal. The transfer of these arguments into the manuscript could still be improved (see below). However, assuming proper treatment of these comments I feel that the authors have brought the manuscript to a level that is suitable for Nature Communications. No further review required from my side.

(Re) We acknowledge the positive evaluation of the reviewer. We provide our specific responses to the further comments and concerns below.

(Comment #1) The partial preservation of order in the Ba-leached BaIrNbO_x material is a very interesting point, that has strong implications for the usefulness of employing (unstable) precursor materials such as perovskites to create stable “activated” catalysts. It shows that the nature of the precursor really matters, not only for the openness of the morphology of the ensuing IrO_x catalysts (which seemed to be the case in most previous studies with perovskite or IrNi precursors), but also for the crystal structure. I feel that the authors should highlight this more in the text, e.g. in abstract and/or introduction.

(Re) One of the key results in this work is that highly ionic bonding characteristics of Nb⁵⁺ with oxygen make a critical contribution to inhibiting lattice oxygen participation during the OER without disturbing the stable [Ir₃O₁₂] trimers. In particular, a combination of atomic-scale STEM, TOF SIMS, and XAS demonstrated the important role of substantially suppressing the lattice oxygen oxidation. We thus believe that this main message will be clearly conveyed to readers.

(Comment #2) As I mentioned before, the stabilizing effect of Nb and Ta in IrO_x has been previously established. In their rebuttal, the authors clearly discuss the difference between their work and what was done before. I feel that this discussion was not very clear in the manuscript, however.

(Re) To clarify the exact role of Nb and Ta in the lattice for suppressing lattice oxygen activation rather than existing as second phases, we included further explanations on page 8 in the main text of the manuscript, as provided below.

As demonstrated in a previous study on the phase relations of TiO₂–IrO₂ and SnO₂–IrO₂⁹², it is noted that solubility limits of insulating TiO₂ and SnO₂ into metallic IrO₂ are very low (less than 5% at 900 °C), even though the valence state of Ti⁴⁺, Sn⁴⁺, and Ir⁴⁺ is identical and even the crystal structure of TiO₂, SnO₂, and IrO₂ is the same rutile structure. Because the crystal structure of Nb₂O₅ and the chemical bonding nature of Nb–O completely differ from the crystal structure of IrO₂ and the bonding characteristics of Ir–O, the solubility of Nb is thus difficult to exceed 10%. To directly prove this considerably low solubility of Nb in rutile IrO₂, we carried out an additional X-ray diffraction analysis using a powder mixture of 75IrO₂–25NbO_{2.5} annealed at 800 °C for a sufficiently long period of time, 100 h, in air. As directly shown in Supplementary Fig. 34, the diffraction result verifies the appearance of the high-intensity Bragg reflections for the secondary Nb₂O₅ phase, demonstrating that the solubility of Nb in rutile IrO₂ is considerably low (evidently less than 10% based on the diffraction pattern). In this respect, attaining the 25% solubility of Nb and Ta in the 12R-type iridate and directly

visualizing its ordered configuration are other significant findings in this work.

(Comment #3) The capacitance measurements in supplementary figure 24 actually address my concern regarding the possibility of particle detachment as one of the reasons for degradation.

(Re) As demonstrated in the EDS maps, Mn, Co, Ni, and In rapidly leach out during anodic cycling, leading to unavoidable lattice collapse. Consequently, as the reviewer pointed out, we agree that particle detachment can be induced by lattice collapse and subsequent dissolution in these solid solutions, thereby accelerating the reduction of DL capacitance. However, we would like to note that ‘particle detachment’ is not the cause of catalyst degradation but rather a consequence of lattice dissolution, which is strongly correlated with the degradation.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have addressed my comment properly. The manuscript can be published as is

Reviewer #2 (Remarks to the Author):

The authors have addressed my previous comments in a satisfactory fashion. In particular, discovering the oxyhydroxide via XPS and using such a structure for the MD renders the results much more plausible. As such I recommend publishing the manuscript in Nature Communications without further changes.

Reviewer #3 (Remarks to the Author):

The authors have sufficiently addressed my remaining concerns. I believe that the manuscript is now suitable for publication in Nature Communications.