

Supplementary Information

Directing Ru-based acidic oxygen evolution catalysts toward a universal dual-site pathway

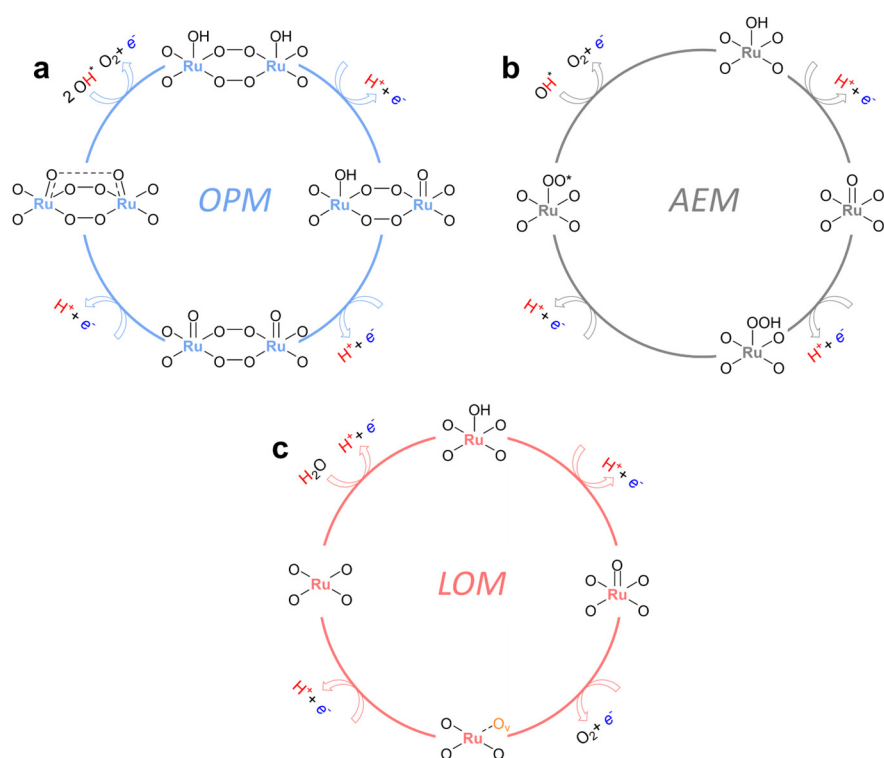
Yingjie Hu¹, Yongde Long¹, Baoguang Mao¹, Zeqiang Yu¹, Linjie Zhao¹, Cheng Tang², Ruitian Kou¹, Chaoyang Sun¹, Chuangang Hu^{1*}

¹State Key Laboratory of Organic-Inorganic Composites, Beijing Key Laboratory of Intelligent Design and Manufacturing for Hydrogen Energy Materials, Beijing University of Chemical Technology, Beijing, China.

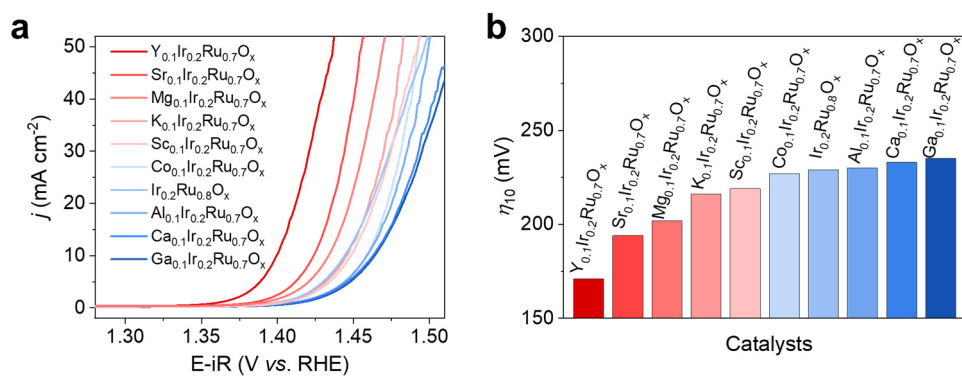
²Tsinghua Centre for Green Chemical Engineering Electrification, State Key Laboratory of Chemical Engineering and Low-Carbon Technology, Department of Chemical Engineering, Tsinghua University, Beijing, China.

*Corresponding author. Email: chuangang.hu@mail.buct.edu.cn

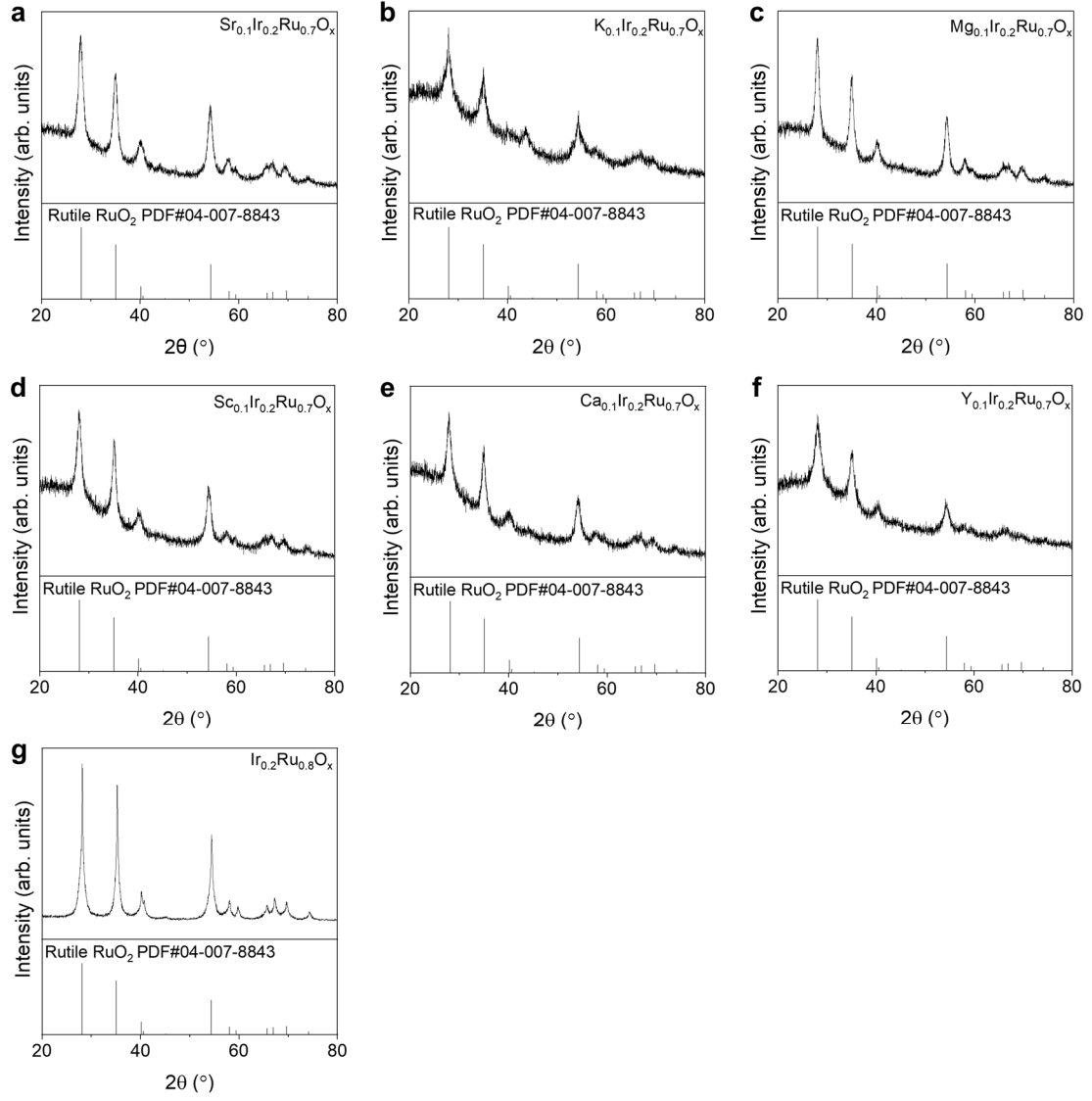
Supplementary Text



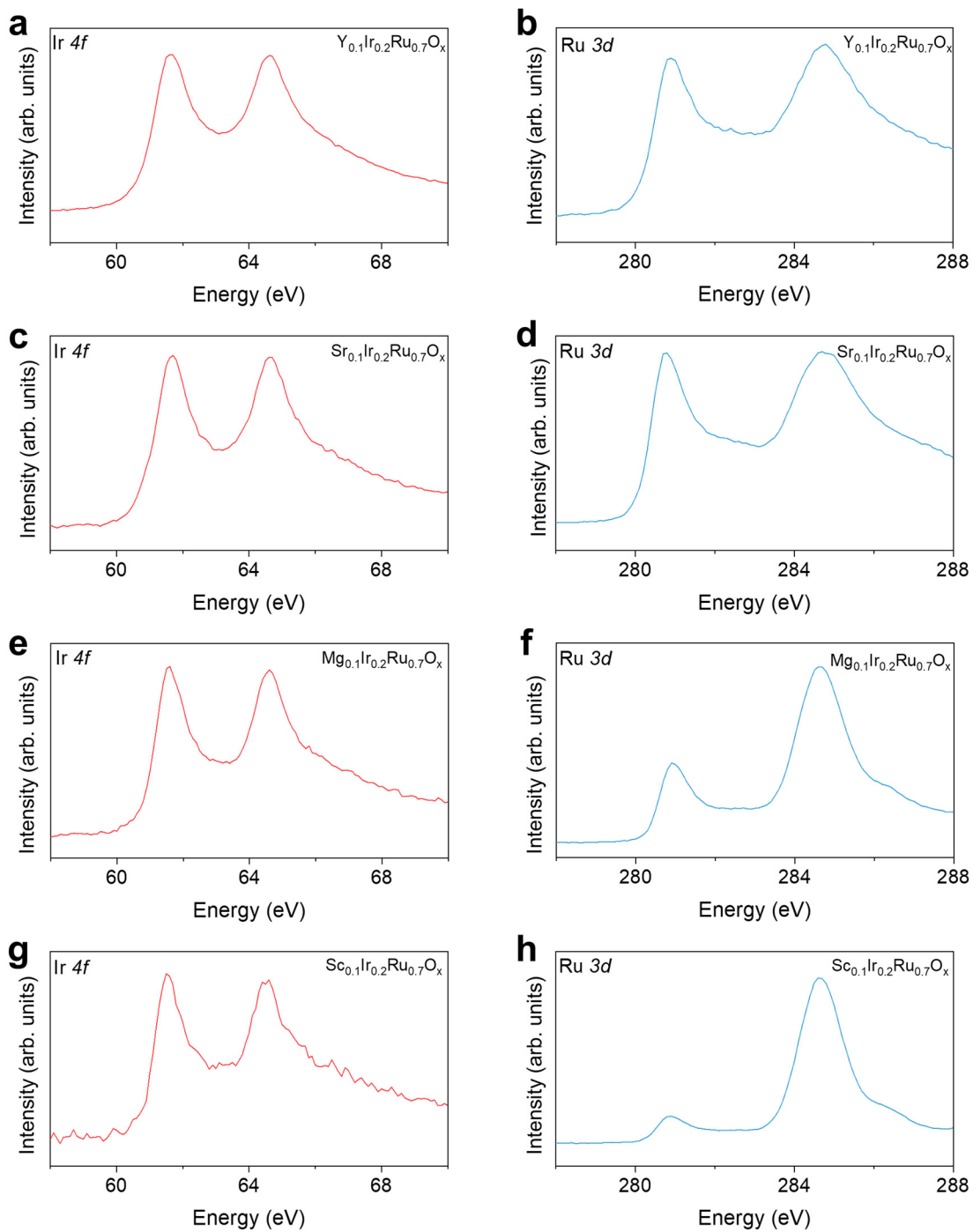
Supplementary Figure 1. (a) OPM, (b) AEM, and (c) LOM pathways on the sites.



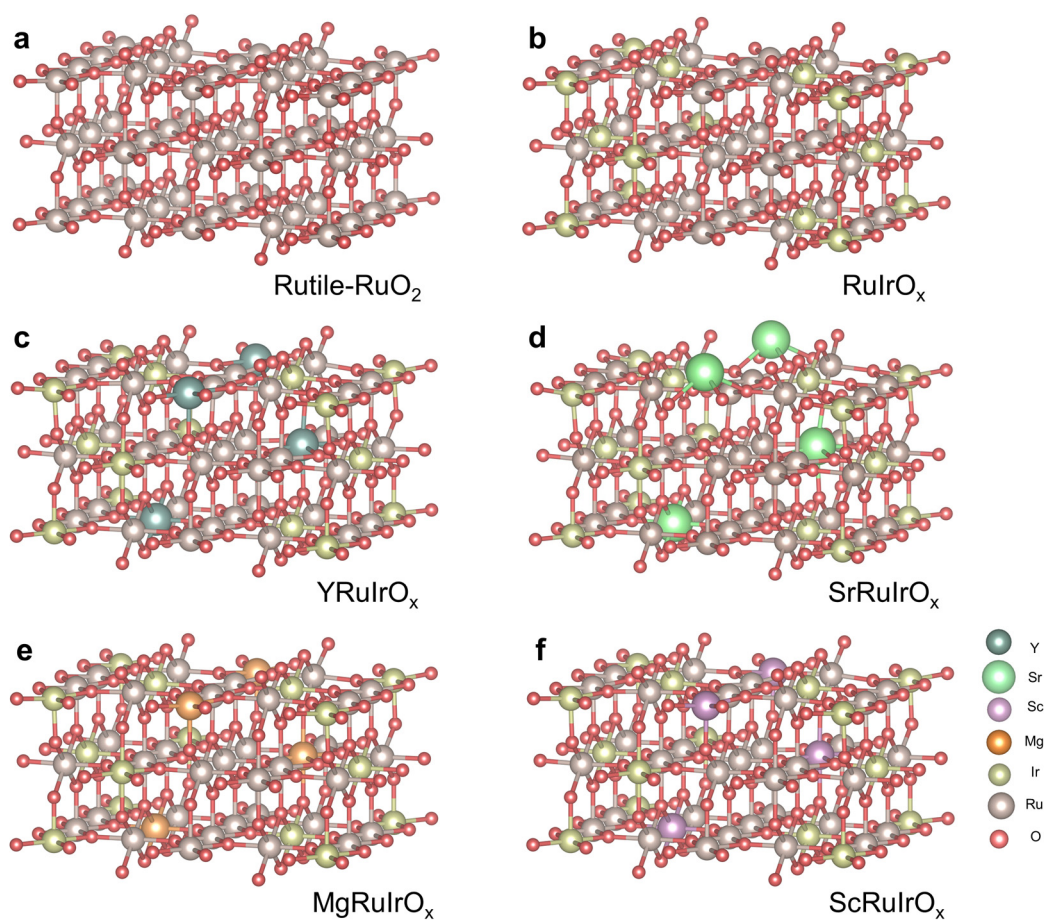
Supplementary Figure 2. (a) LSV curves and (b) overpotential at 10 mA cm^{-2} of $\text{M}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ based catalysts with different metal heteroatoms.



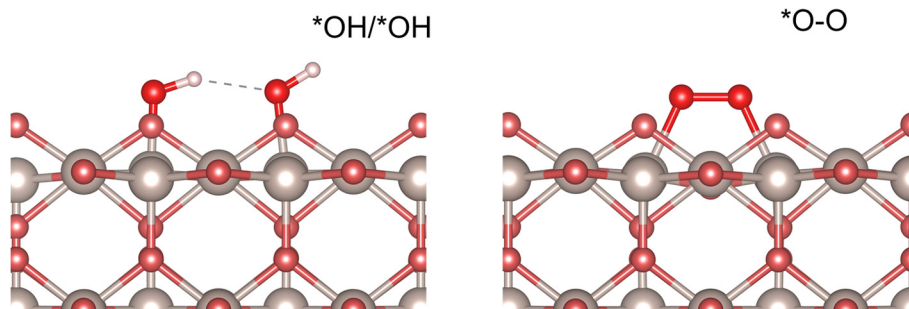
Supplementary Figure 3. XRD patterns of (a) $\text{Sr}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, (b) $\text{K}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, (c) $\text{Mg}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, (d) $\text{Sc}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, (e) $\text{Ca}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, (f) $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, and (g) $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$.



Supplementary Figure 4. Ru *3d* and Ir *4f* XPS spectra of $M_{0.1}Ir_{0.2}Ru_{0.7}O_x$ samples. (a, b) $Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$, (c, d) $Sr_{0.1}Ir_{0.2}Ru_{0.7}O_x$, (e, f) $Mg_{0.1}Ir_{0.2}Ru_{0.7}O_x$, and (g, h) $Sc_{0.1}Ir_{0.2}Ru_{0.7}O_x$.

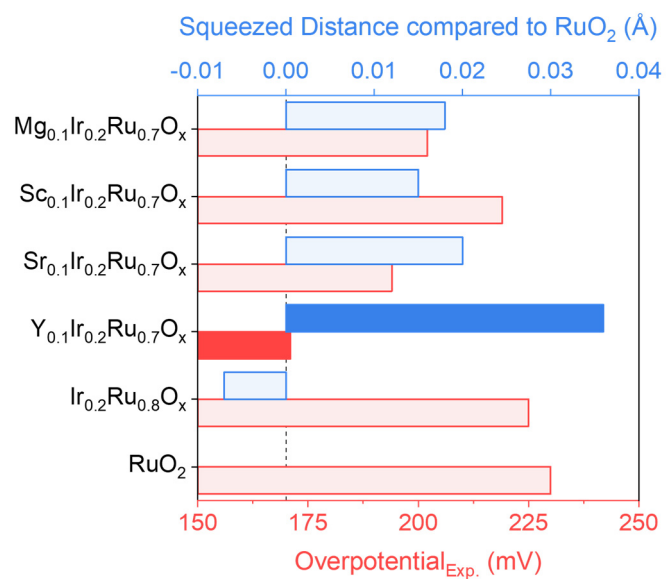


Supplementary Figure 5. Atomic structures of (a) Rutile-RuO₂, (b) RuIrO_x, (c) YRuIrO_x, (d) SrRuIrO_x, (e) MgRuIrO_x, and (f) ScRuIrO_x.

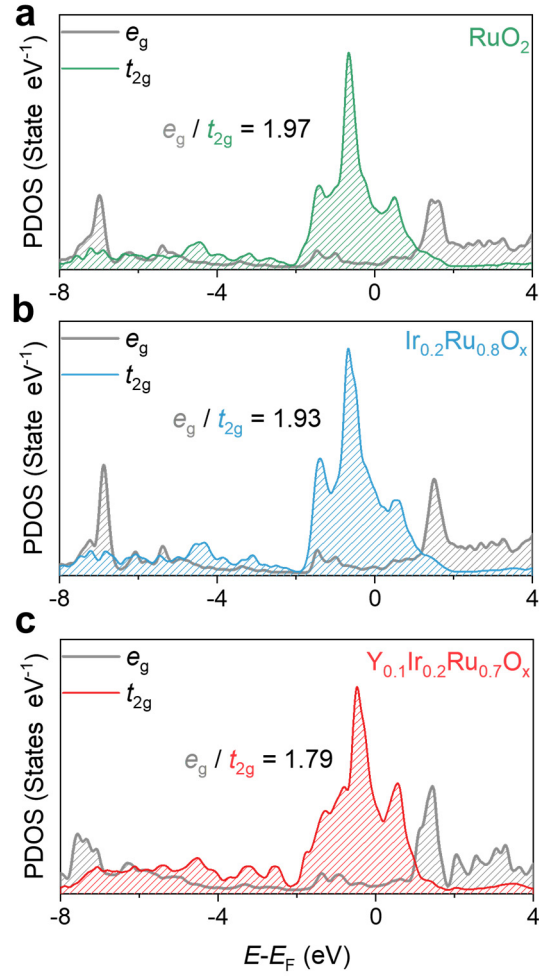


Supplementary Figure 6. O-O coupling step of dual sites pathway on Rutile-RuO₂ model.

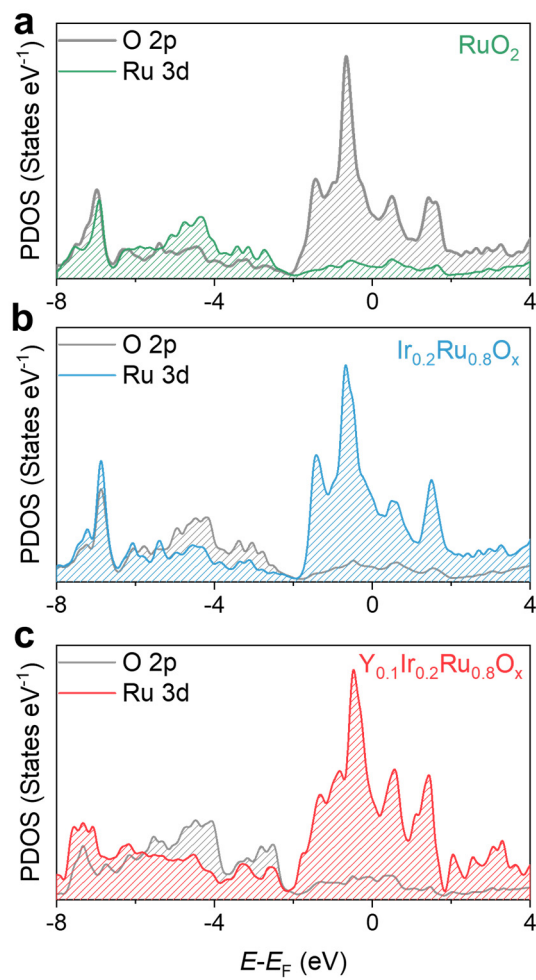
The coupling of the -O-O*- intermediate may not always serve as the rate-determining step in final energy barrier calculations when appropriate adjacent-site distances are achieved, it remains exceedingly challenging without actively manipulating the Ru-Ru₁ bond length. Hence, prior investigation into lowering the activation energy of coupling step to an appropriate range through bond-length engineering is essential for selectively facilitating this reaction step. Notably, the calculation presented in Fig. 1c is based on this process. By modulating the degree of compression in the standard Rutile-RuO₂ model, the free energy differences between the relevant steps were computed at the specified Ru-Ru₁ bond lengths, yielding the results shown in Fig. 1c.



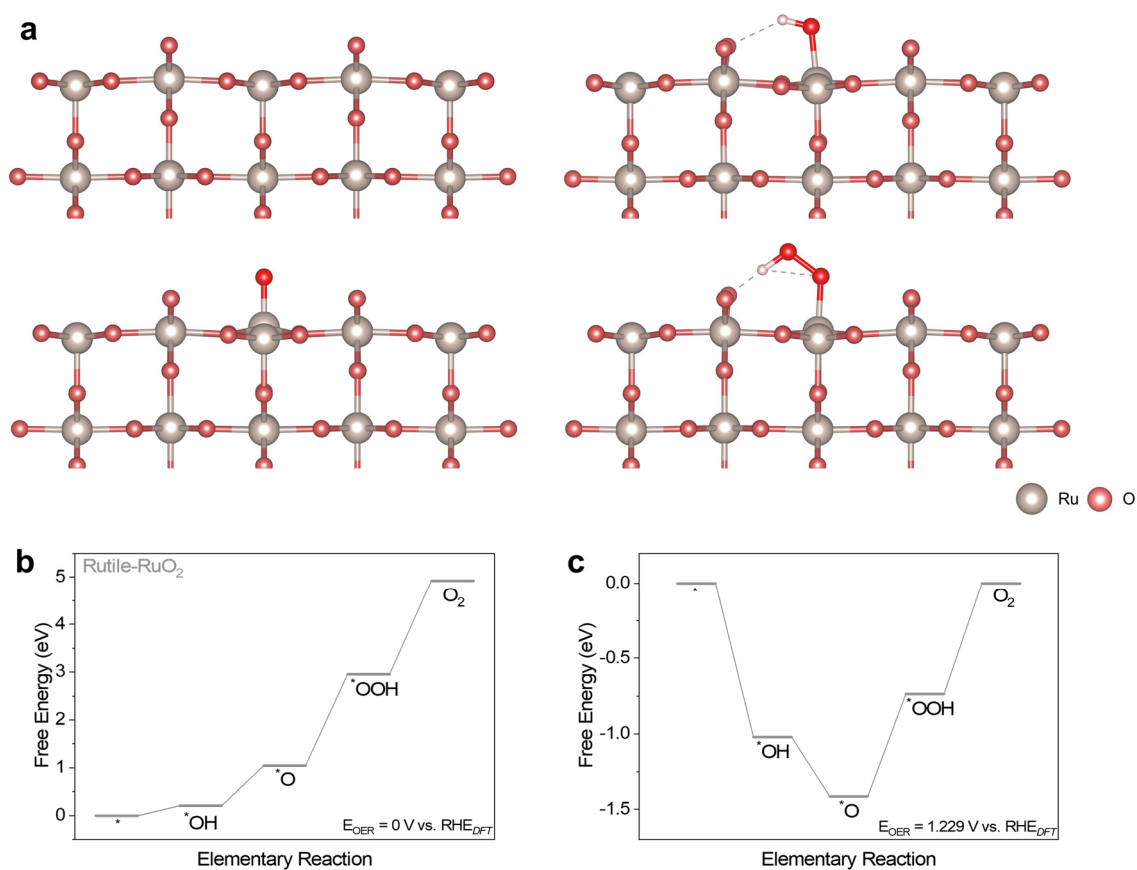
Supplementary Figure 7. The correlation between the degree of lattice compression in the $\text{M}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ and RuO_2 and their corresponding overpotentials at 10 mA cm^{-2} .



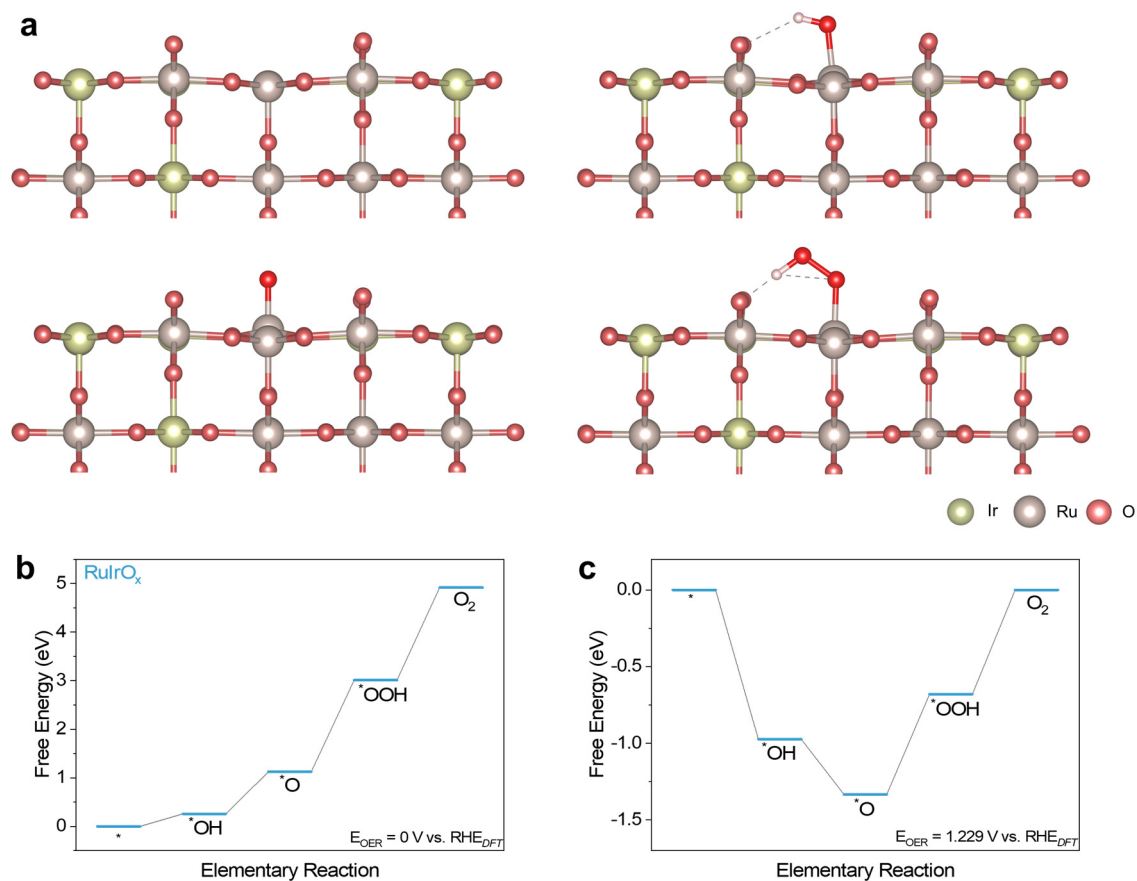
Supplementary Figure 8. Crystal-orbital-resolved PDOS plots for (a) RuO_2 , (b) $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$, and (c) $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$.



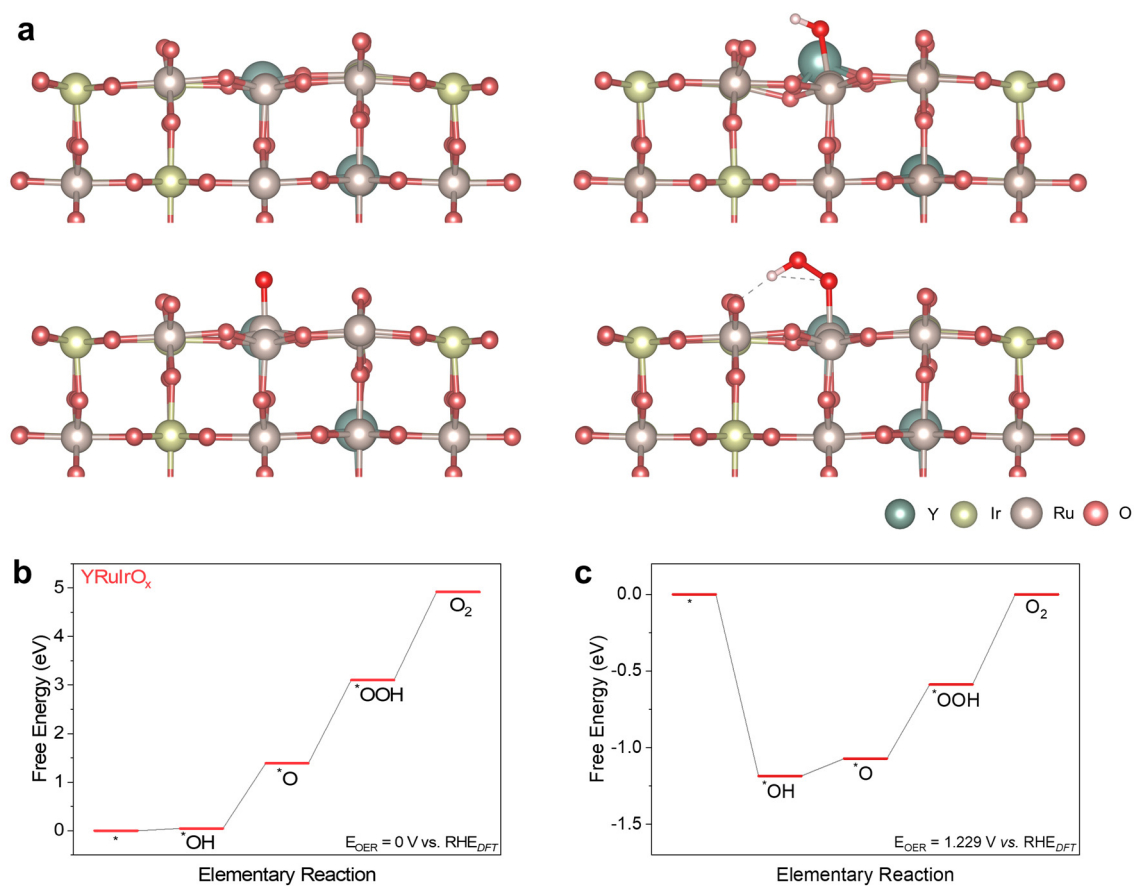
Supplementary Figure 9. Element-specific, orbital-projected PDOS plots for (a) RuO₂, (b) Ir_{0.2}Ru_{0.8}O_x, and (c) Y_{0.1}Ir_{0.2}Ru_{0.7}O_x.



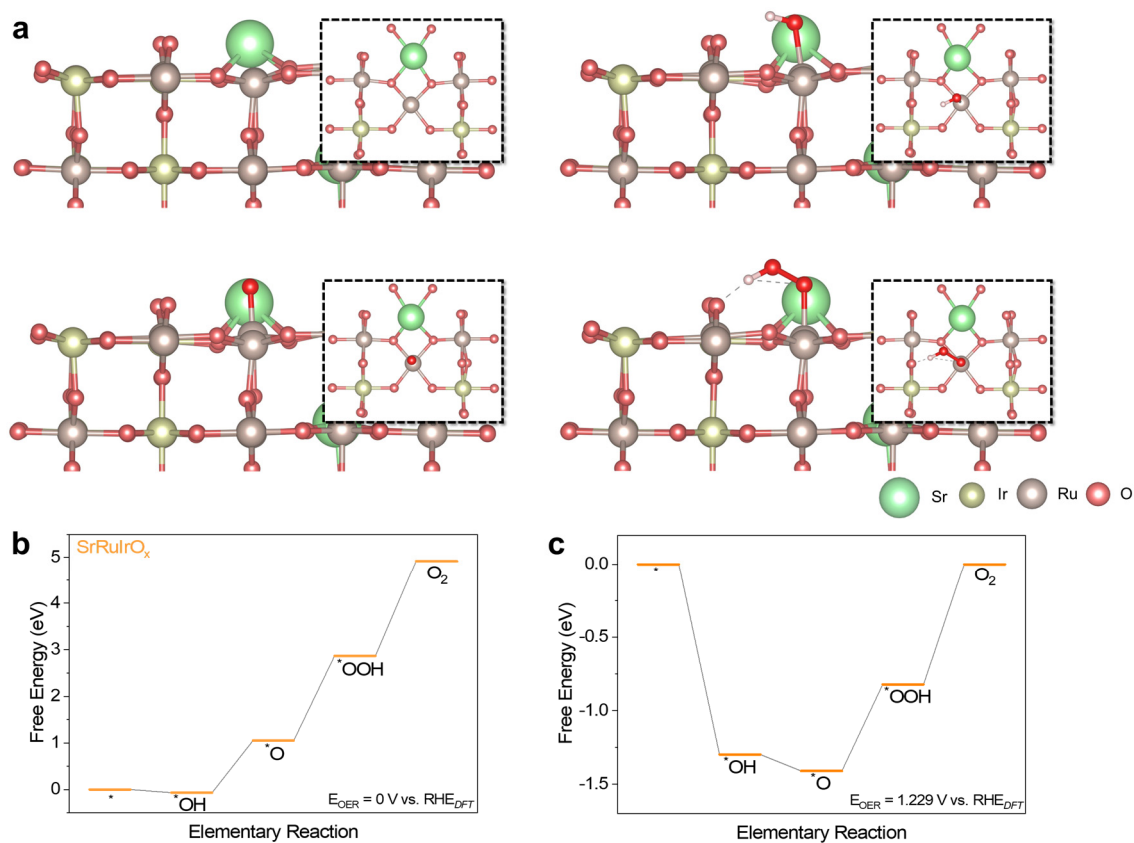
Supplementary Figure 10. (a) DFT-calculated models, step diagrams at (b) 0 V vs. RHE and (c) 1.229 V vs. RHE via AEM, both without H^{*} desorption on the Rutile-RuO₂ (110) surface.



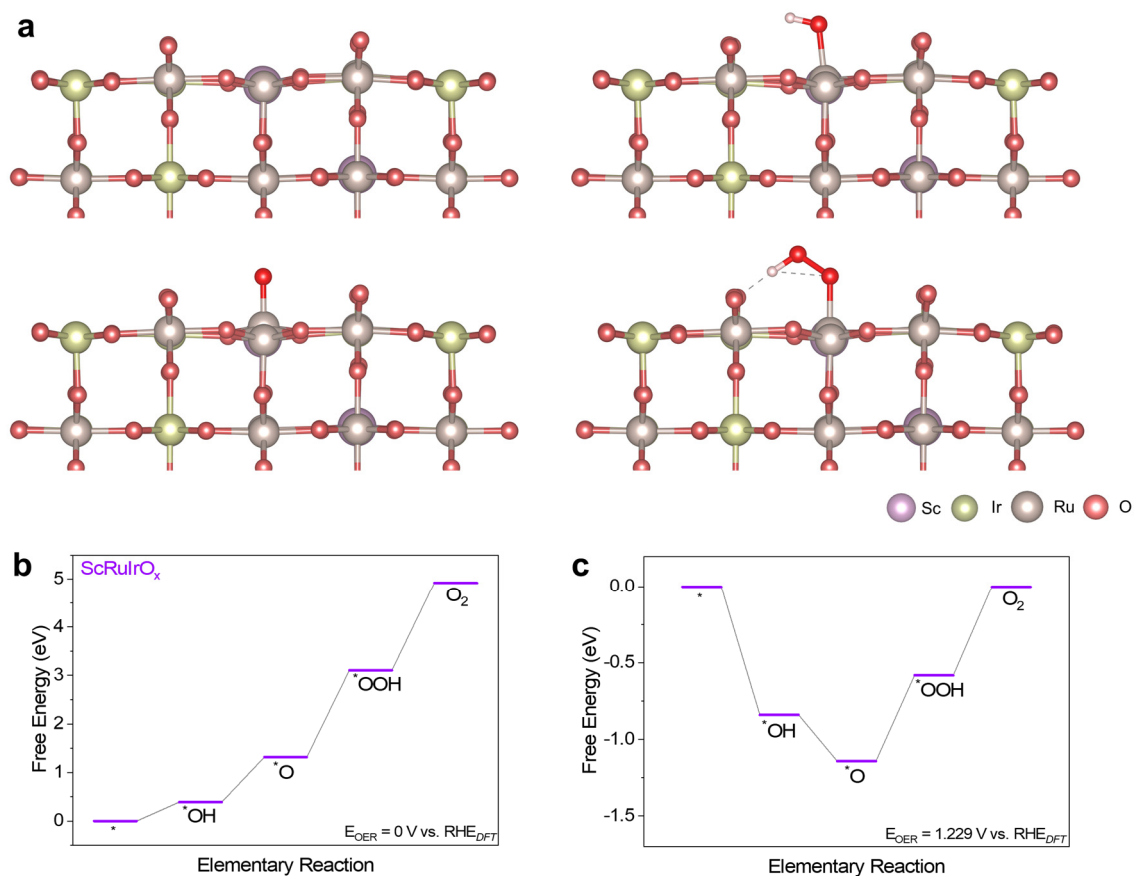
Supplementary Figure 11. (a) DFT-calculated models, step diagrams at (b) 0 V vs. RHE and (c) 1.229 V vs. RHE via AEM, both without H⁺ desorption on the RuIrO_x (110) surface.



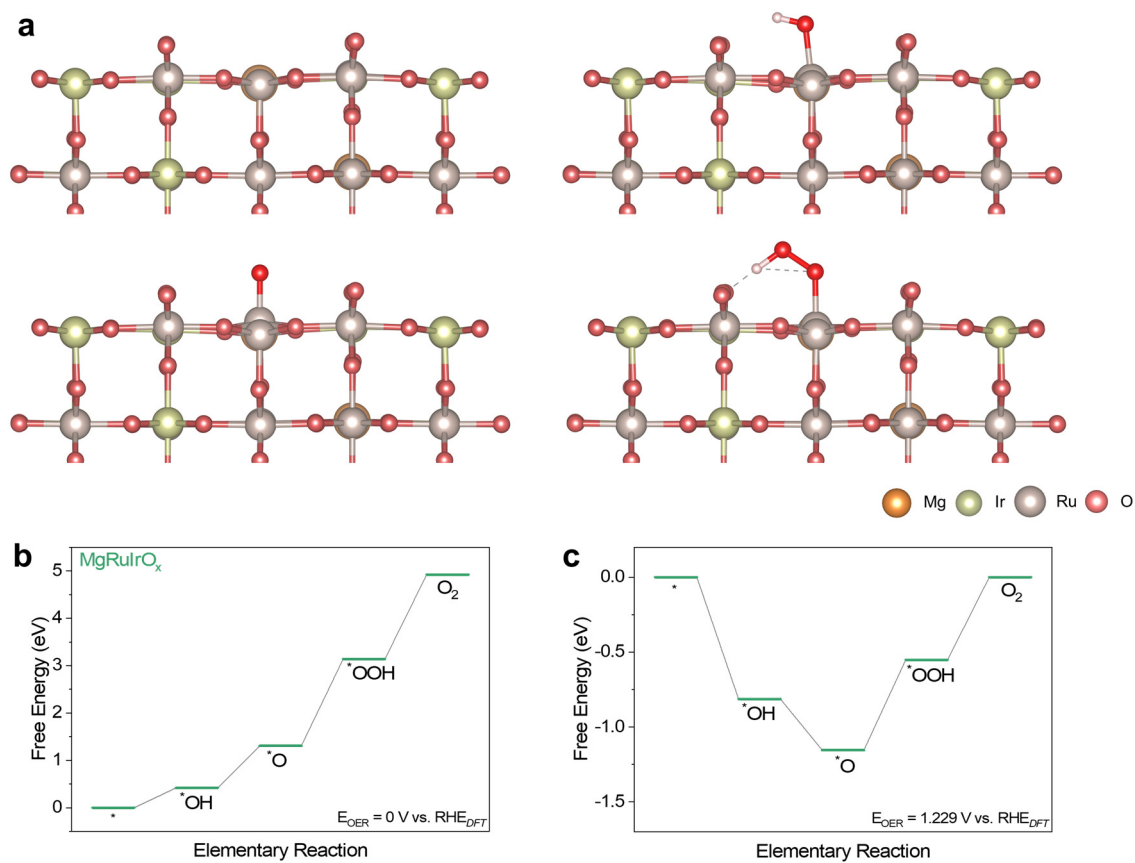
Supplementary Figure 12. (a) DFT-calculated models, step diagrams at (b) 0 V vs. RHE and (c) 1.229 V vs. RHE via AEM, both without H^{*} desorption on the YRuIrO_x (110) surface.



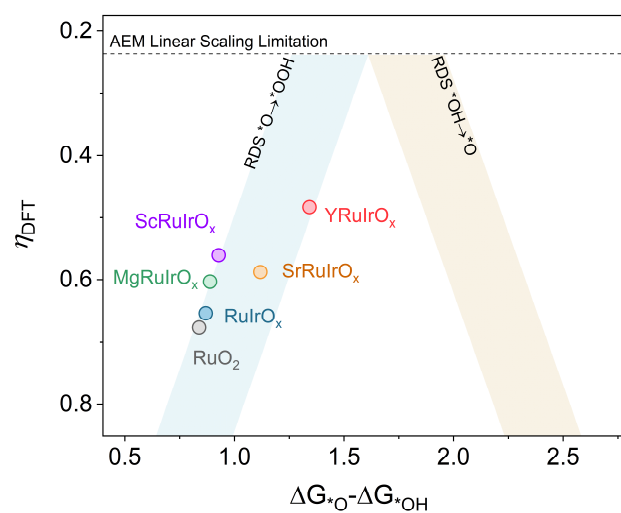
Supplementary Figure 13. (a) DFT-calculated models, step diagrams at (b) 0 V vs. RHE and (c) 1.229 V vs. RHE via AEM, both without H⁺ desorption on the SrRuIrO_x (110) surface.



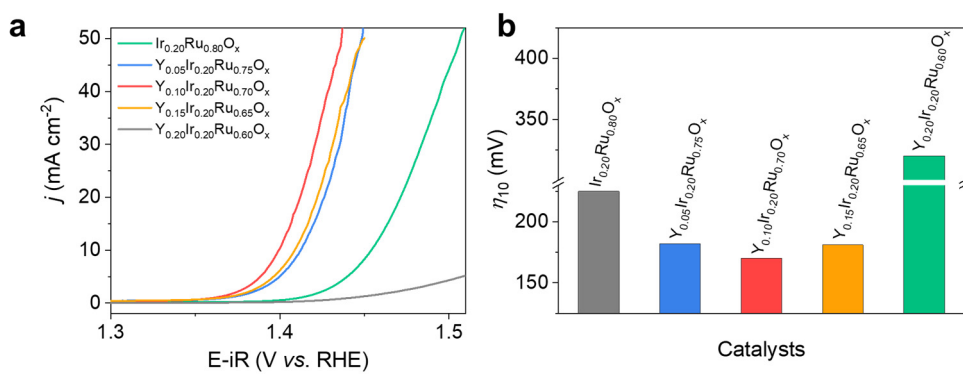
Supplementary Figure 14. (a) DFT-calculated models, step diagrams at (b) 0 V vs. RHE and (c) 1.229 V vs. RHE via AEM, both without H⁺ desorption on the ScRuIrO_x (110) surface.



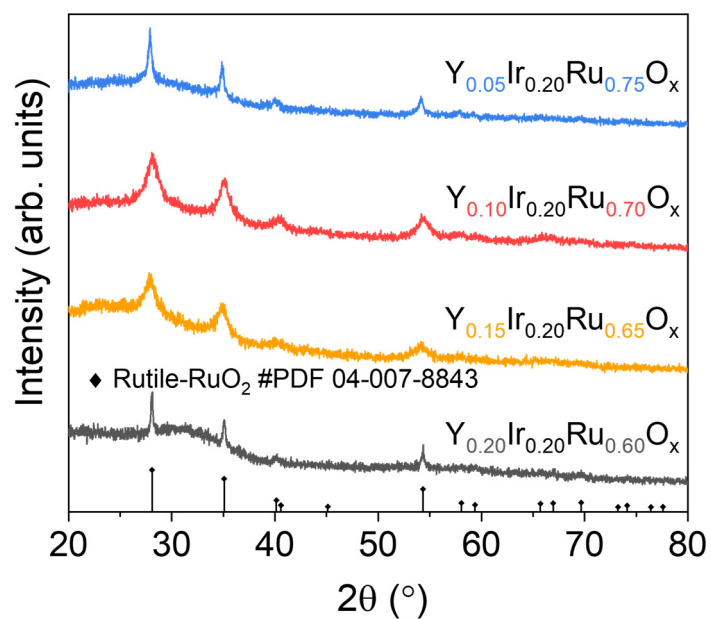
Supplementary Figure 15. (a) DFT-calculated models, step diagrams at (b) 0 V vs. RHE and (c) 1.229 V vs. RHE via AEM, both without H^* desorption on the MgRuIrO_x (110) surface.



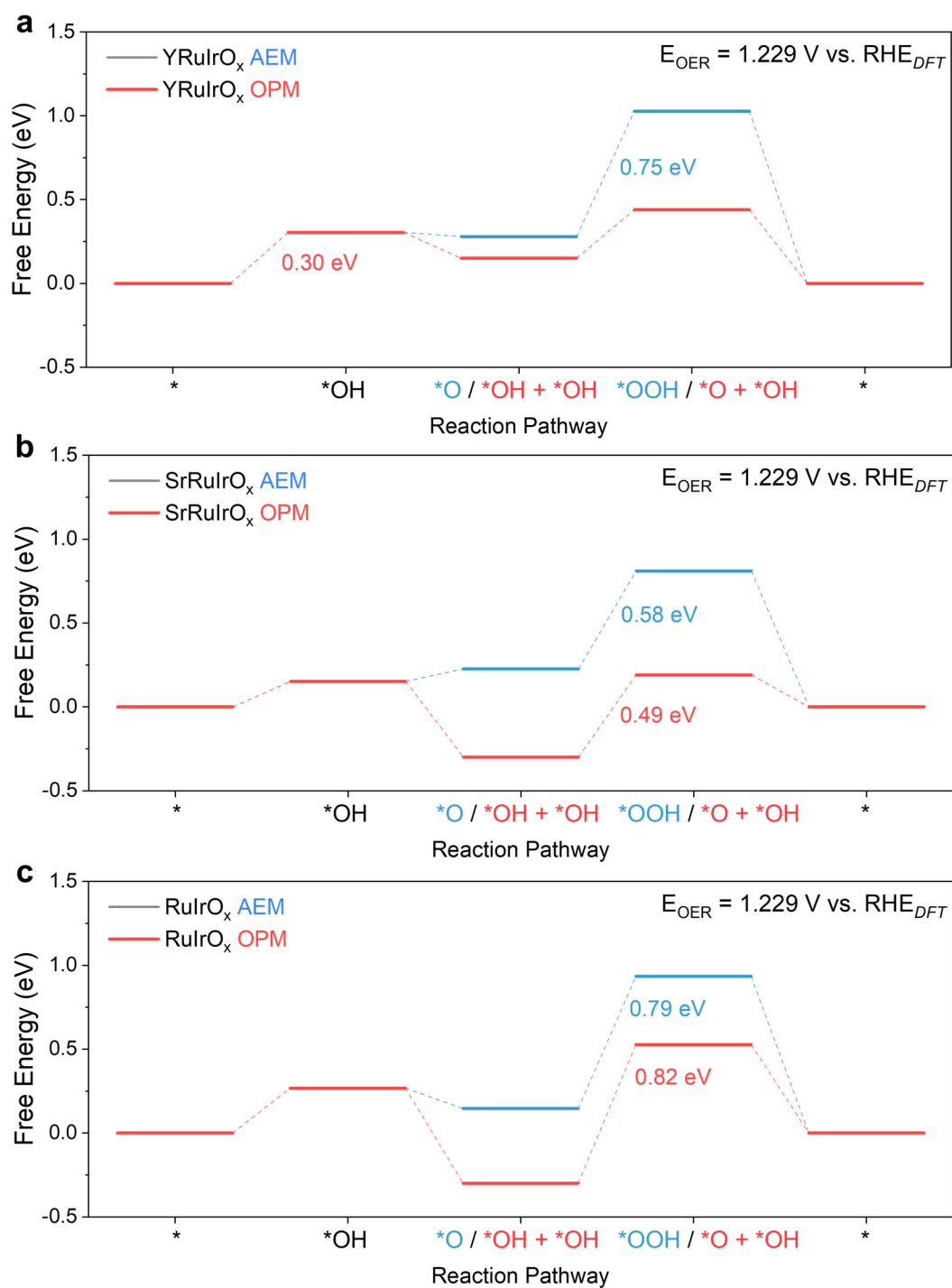
Supplementary Figure 16. AEM-based overpotential volcano plot for MRuIrO_x compositions.



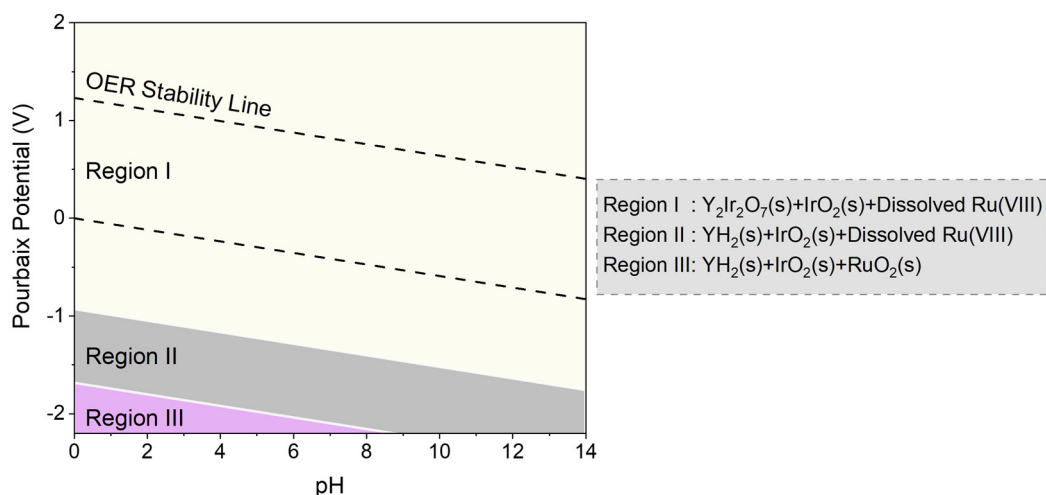
Supplementary Figure 17. (a) LSV curves and (b) overpotentials at 10 mA cm⁻² of $\text{Y}_z\text{Ir}_{0.20}\text{Ru}_{0.80-z}\text{O}_x$ catalysts with varied z content ($z = 0-0.20$), illustrating the effect of Y doping on OER activity.



Supplementary Figure 18. XRD patterns of $\text{Y}_{0.05}\text{Ir}_{0.20}\text{Ru}_{0.75}\text{O}_x$, $\text{Y}_{0.10}\text{Ir}_{0.20}\text{Ru}_{0.70}\text{O}_x$, $\text{Y}_{0.15}\text{Ir}_{0.20}\text{Ru}_{0.65}\text{O}_x$, and $\text{Y}_{0.20}\text{Ir}_{0.20}\text{Ru}_{0.60}\text{O}_x$.

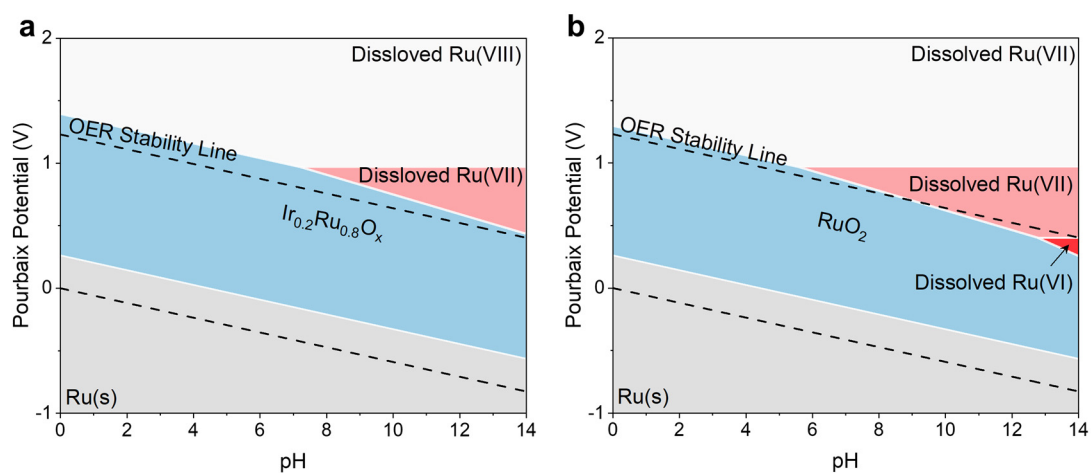


Supplementary Figure 19. Free-energy step diagram of (a) YRuIrO_x (b) SrRuIrO_x, and (c) RuIrO_x at 1.229 V vs. RHE via AEM and OPM pathways.

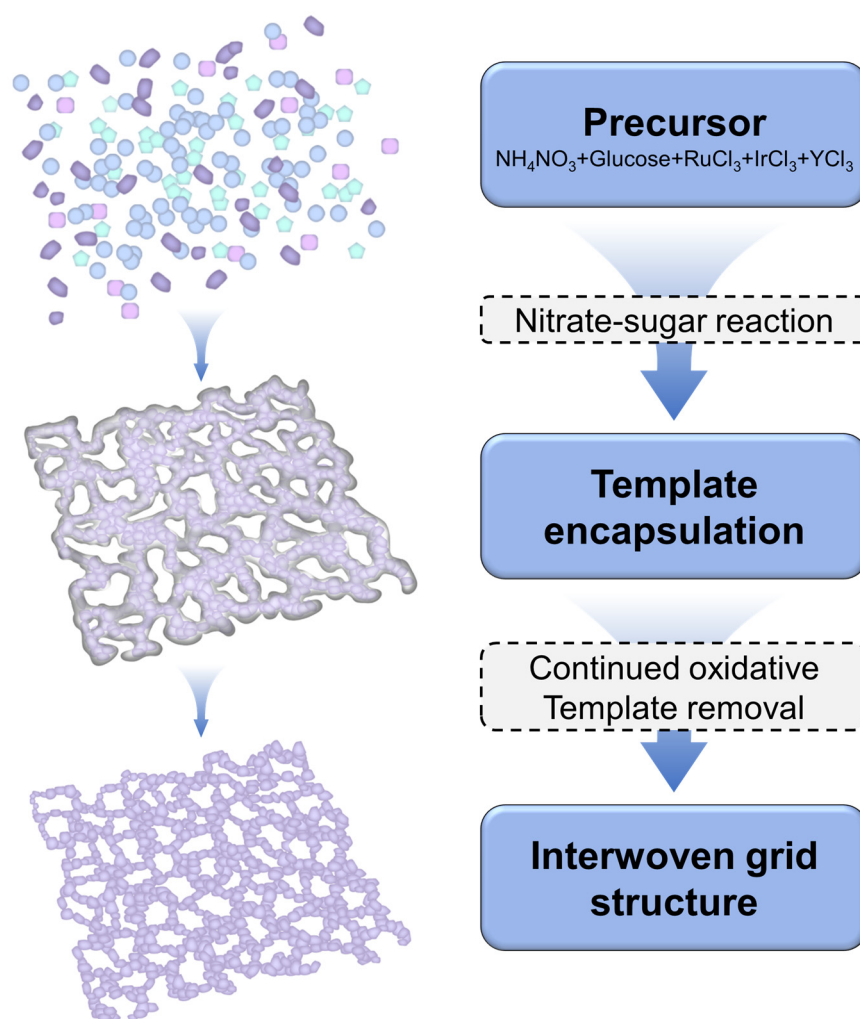


Supplementary Figure 20. Pourbaix diagram showing the thermodynamic stability regions of Y-, Ir-, and Ru-containing species in $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$.

Note: Because the Pourbaix diagram represents only the thermodynamic comparison of Gibbs free energies among competing phases, the multicomponent $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ phase does not appear as the thermodynamically most stable species within the OER-relevant region (Region I). Likewise, in the highly reducing potential range below the HER region (Regions II and III), thermodynamically stable alloy or hydride phases are predicted to form. Since these regions lie well outside the practical OER operating window, they are not discussed further in this work.

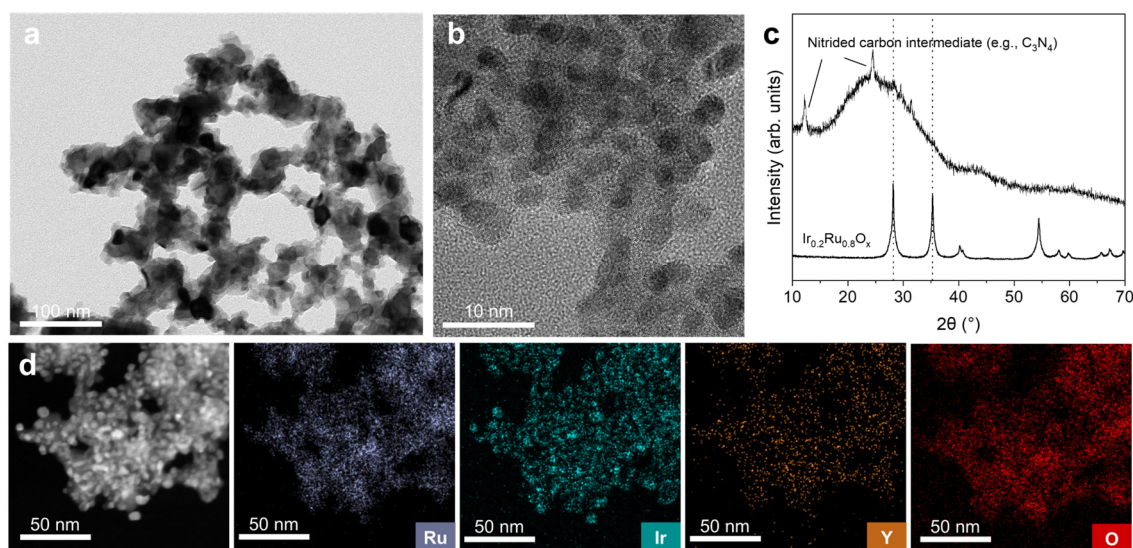


Supplementary Figure 21. Thermodynamically derived Pourbaix diagrams: (a) $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$ and (b) RuO_2 .

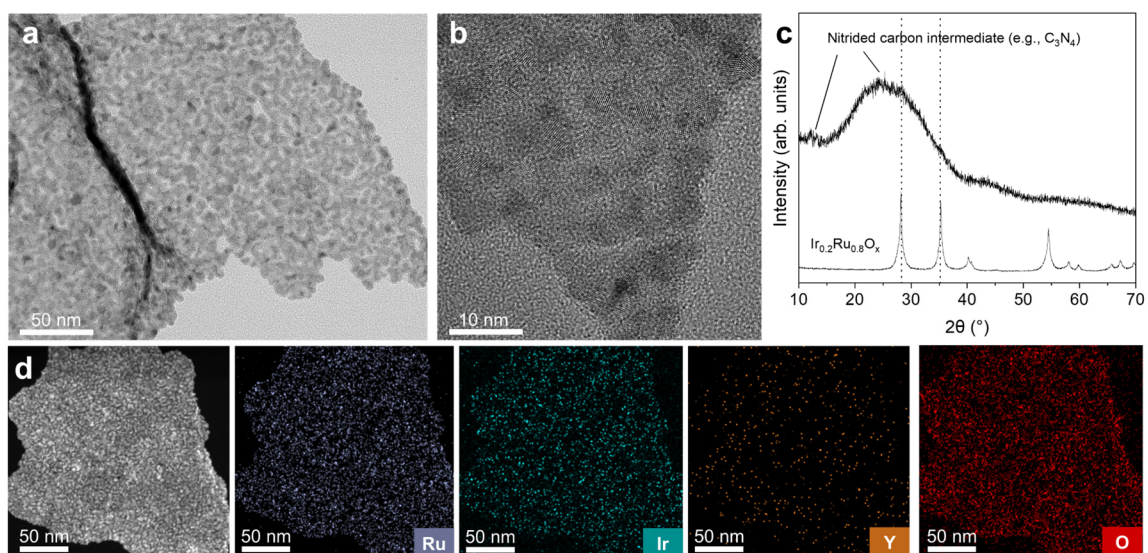


Supplementary Figure 22. Schematic illustration of the synthesis process for $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$.

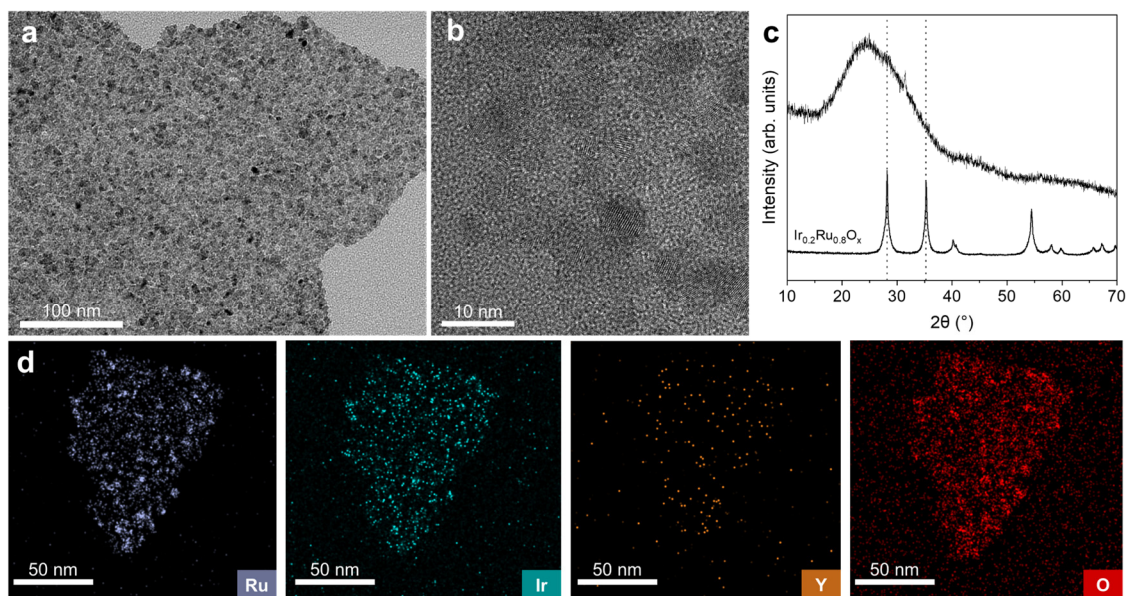
The synthesis process can be described as the conversion of precursors into relatively stable oxidation states, facilitated by a mildly oxidant-rich mixture of ammonium nitrate and glucose. In this process, a nitrate-sugar reaction¹ rapidly carbonizes the glucose-derived carbon substrate under the given temperature, forming a sheet-like template with metal species. The excess oxidant subsequently gradually oxidizes the carbonized substrate while maintaining. During this stage, the metal salt-derived particles connect with each other in the presence of carbon to form a mesoporous network structure (Fig. 2b in the main text). The encapsulating carbon layers are gradually removed and eventually dissociated under the oxidative environment.



Supplementary Figure 23. (a, b) TEM images under different magnifications, (c) XRD pattern, (d) direct area image, and (e) corresponding EDS mappings of the $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ intermediate obtained 1 min after the onset of synthesis.

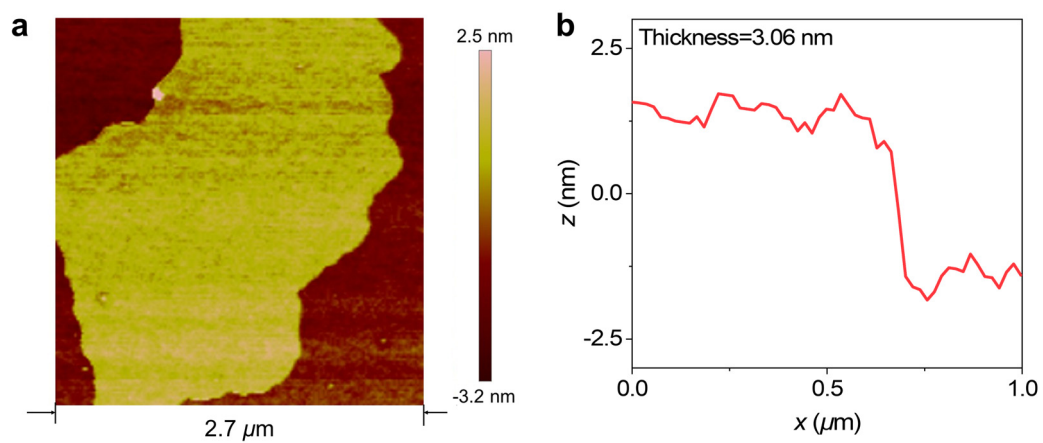


Supplementary Figure 24. (a, b) TEM images under different magnifications, (c) XRD pattern, (d) direct area image, and (e) corresponding EDS mappings of the $Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$ intermediate obtained 3 min after the onset of synthesis.

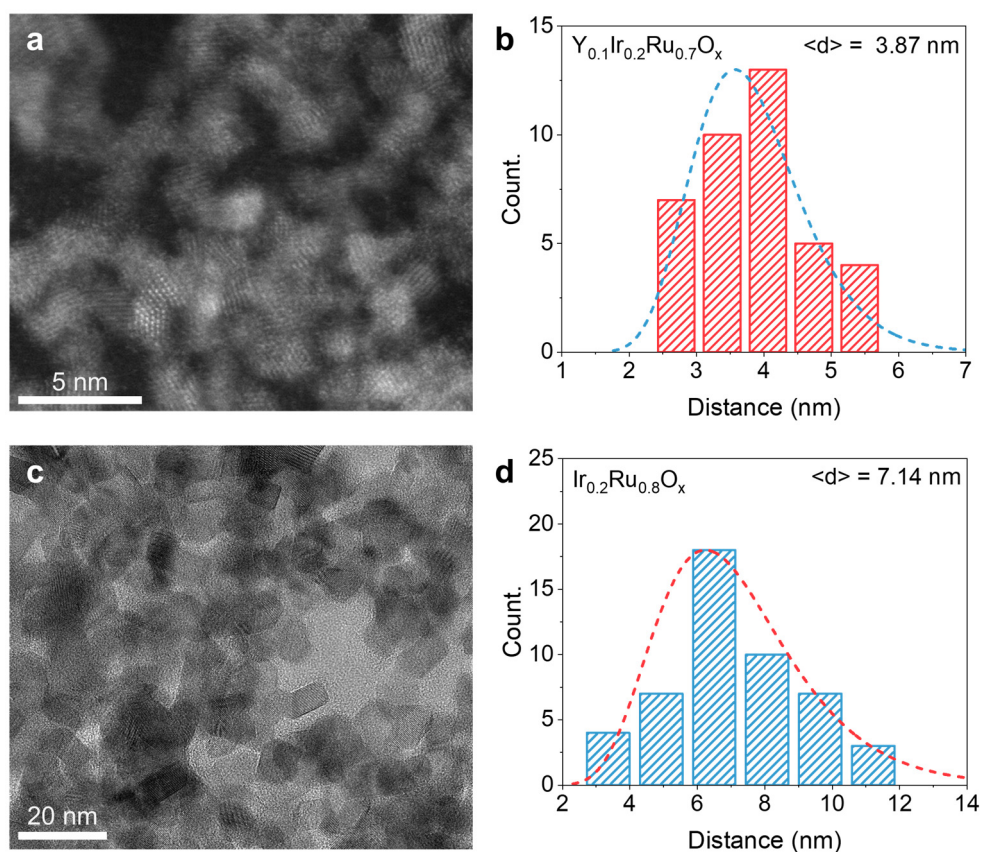


Supplementary Figure 25. (a, b) TEM images under different magnifications, (c) XRD pattern, and (d) corresponding EDS mappings of the $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ intermediate obtained 5 min after the onset of synthesis.

TEM images were used to monitor the structural evolution of the catalyst during synthesis. Intermediate samples were quenched in liquid nitrogen and washed at 1, 3, and 5 min after the onset of the nitrate-sugar reaction. At 1 min, the sample exhibited only initial connectivity, with evident nitration features on the surface of the carbon template. By 3 min, the template had spread and flattened across the surface. The XRD data presented in Supplementary Figures 22d-24d are included to more clearly elucidate the structural evolution of intermediates during the synthesis process, rather than to represent the final phase information of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$. Analysis revealed weak signals corresponding to C_3N_4 , which is from the nitrate-sugar reaction, while no atomic-level crystallization of the metal species was observed, indicating an amorphous intermediate state. At 5 min, small nanoparticles began to crystallize, the surface nitration features diminished, and initial signs of crystallinity became detectable.

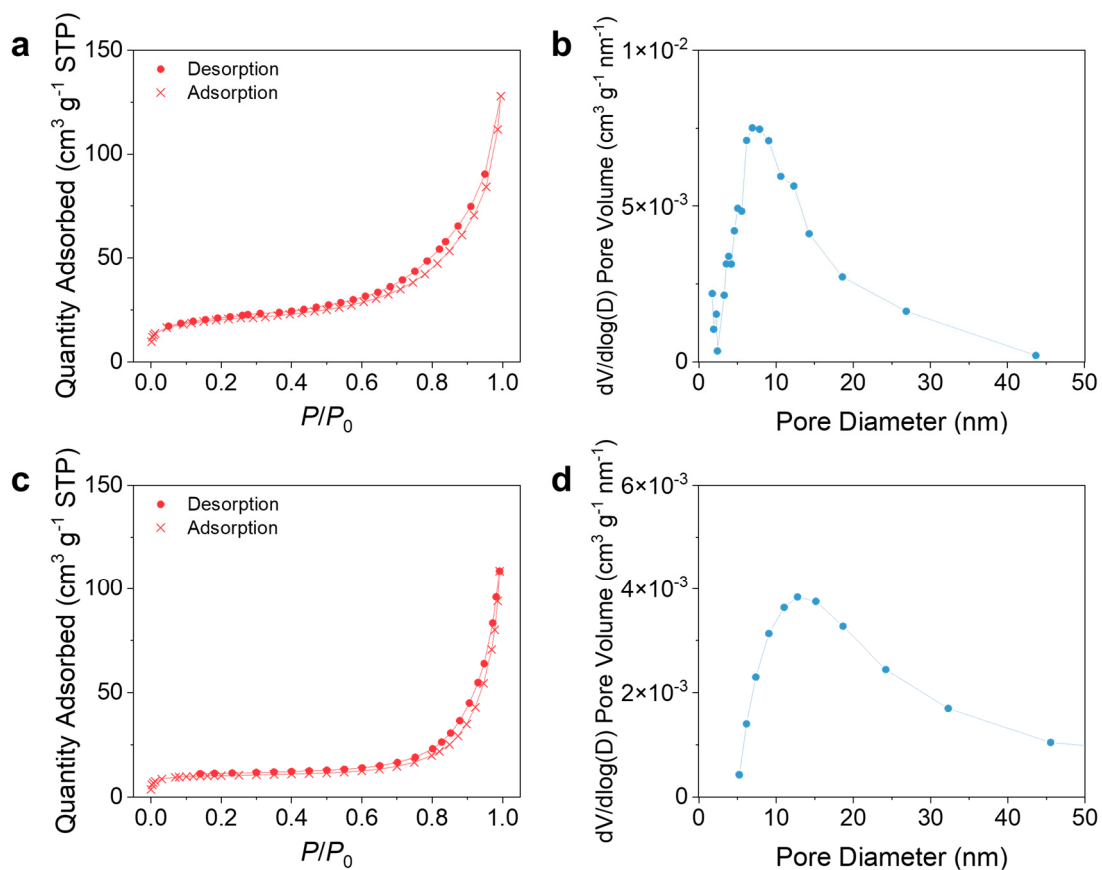


Supplementary Figure 26. (a) AFM image and (b) corresponding thickness profile of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$.



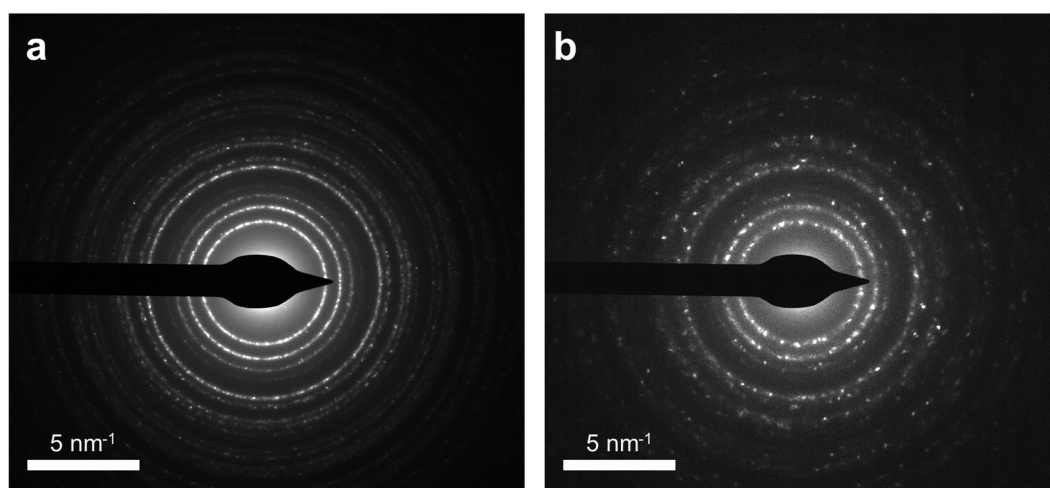
Supplementary Figure 27. (a) TEM image of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ and (b) the corresponding size distribution analysis. (c) TEM image of $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$ and (d) the corresponding size distribution analysis.

Due to the differences in structural disorder, $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ with lower crystallinity formed smaller nanoparticles than $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$.

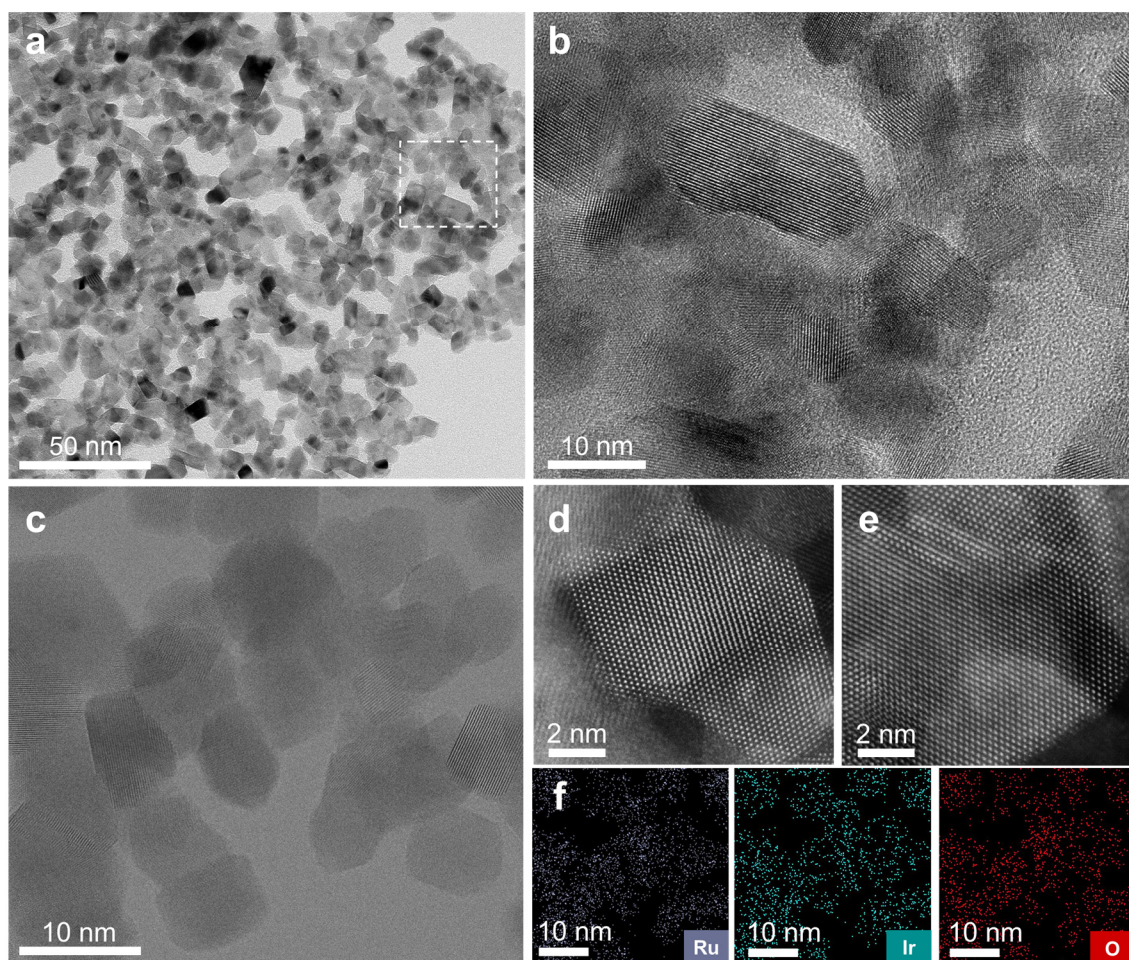


Supplementary Figure 28. (a) BET theory adsorption-desorption isotherms, and (b) corresponding Barrett-Joyner-Halenda method pore size distribution of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$. (c) BET theory adsorption-desorption isotherms, and (d) corresponding Barrett-Joyner-Halenda method pore size distribution of $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$.

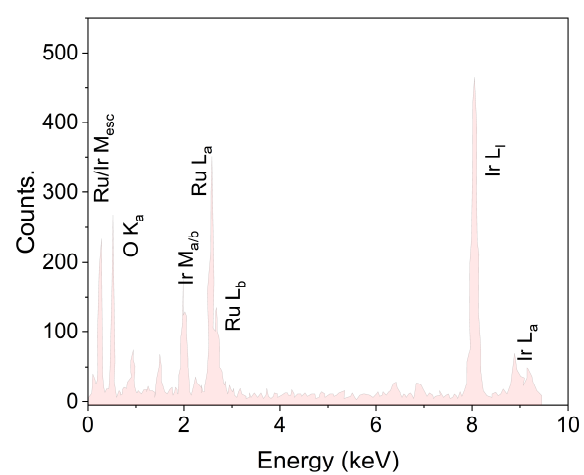
N_2 adsorption-desorption isotherms were obtained at 77 K using a surface area and porosity analyser, after degassing the samples at 300 °C for 8 h under vacuum.



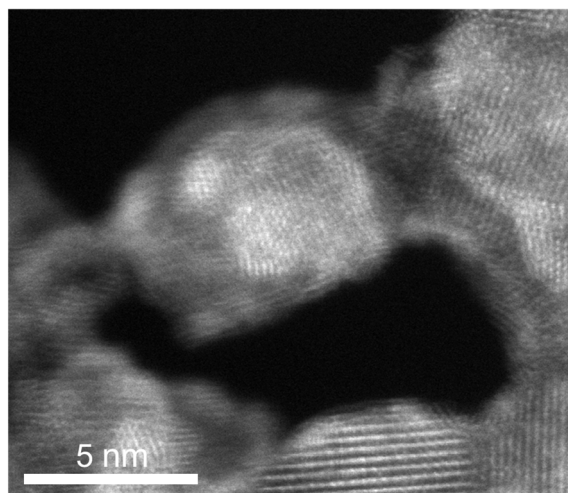
Supplementary Figure 29. SAED patterns of (a) $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$ and (b) $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ for Supplementary Figure 29.



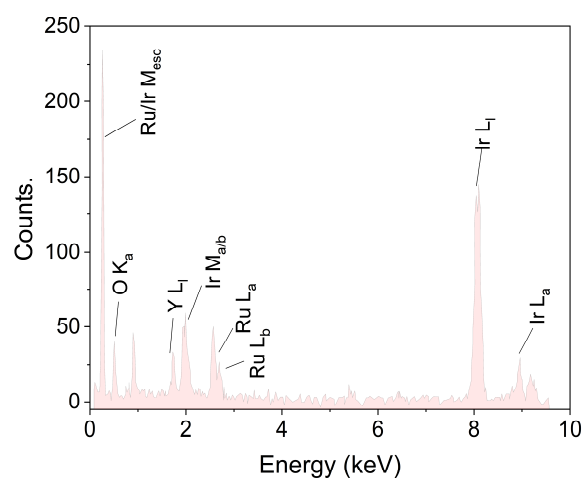
Supplementary Figure 30. (a, b) TEM images and corresponding magnified views of the selected regions for $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$. (c) AC-TEM image and (d, e) AC-TEM images of individual nanoparticles. (f) EDS mappings of the region shown in (c).



Supplementary Figure 31. EDS spectrum from the corresponding elemental-mapping region (Supplementary Figure 30) for Ir_{0.2}Ru_{0.8}O_x.

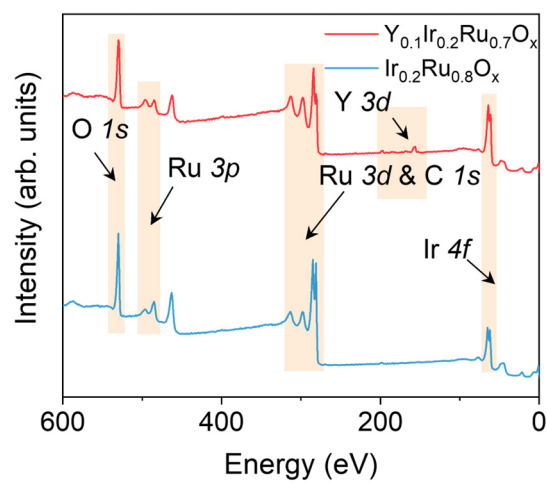


Supplementary Figure 32. ACTEM-EDS image of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ from Fig. 2d.

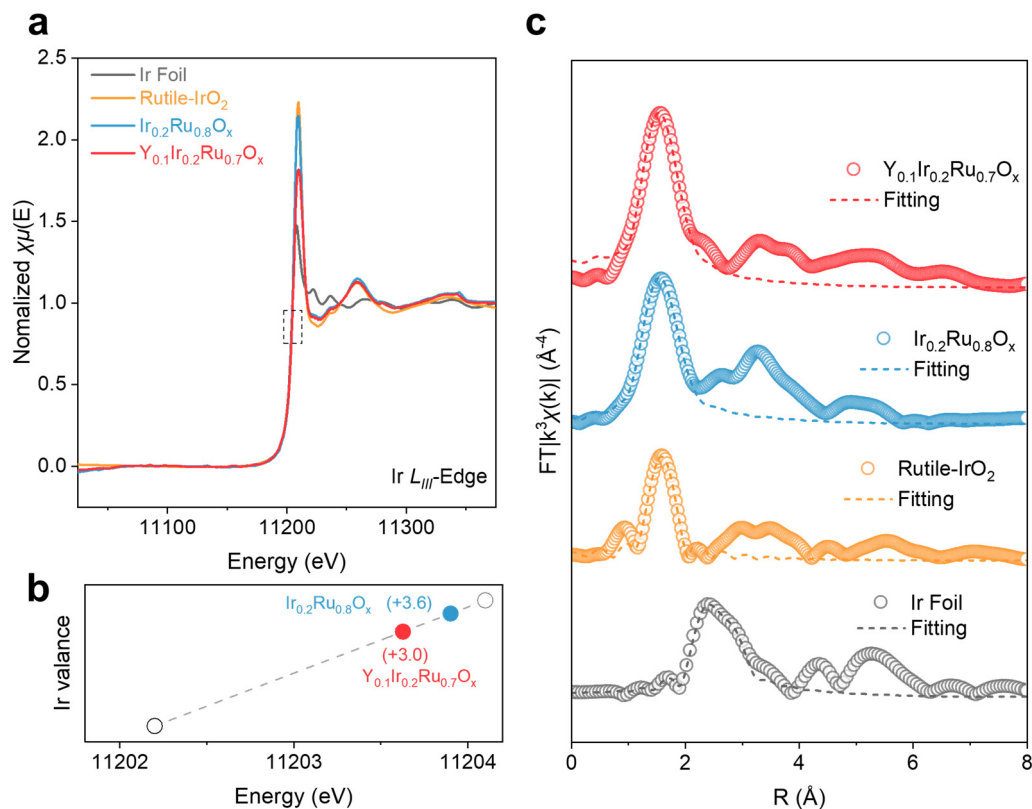


Supplementary Figure 33. EDS spectrum from the corresponding elemental-mapping region (Fig. 2d) for $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$.

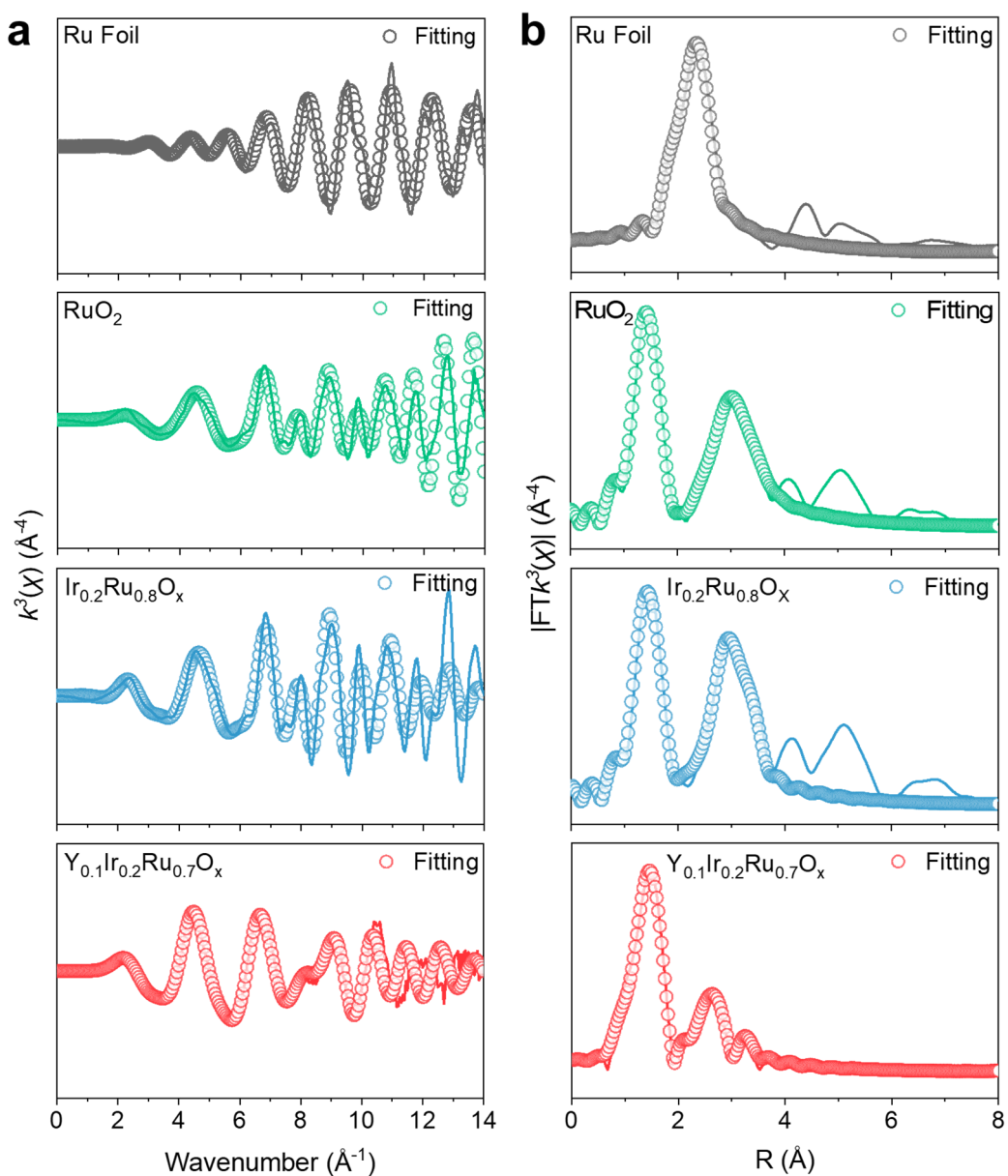
Exploration of Chemical Environment and Configuration



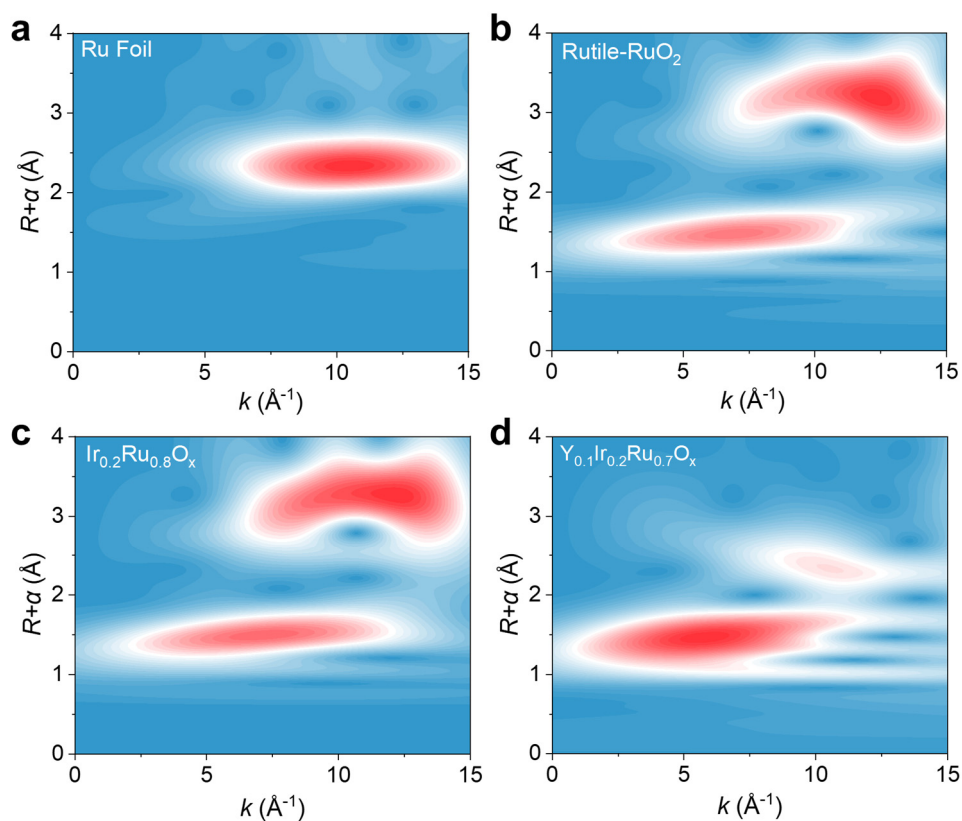
Supplementary Figure 34. XPS spectra of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ and $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$.



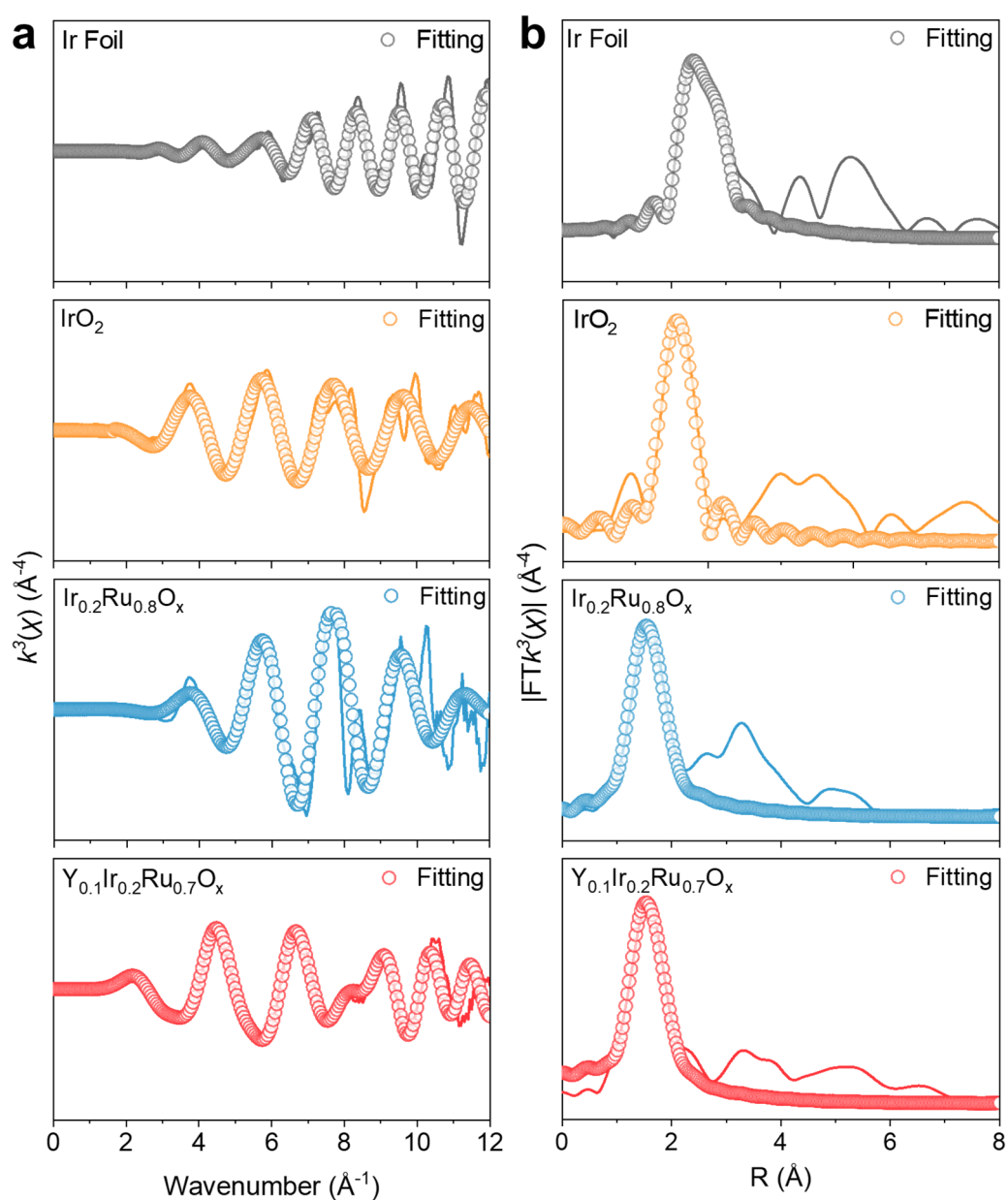
Supplementary Figure 35. Ir L_{III} -edge XAFS data. (a) Normalized XAFS spectra of Y_{0.1}Ir_{0.2}Ru_{0.7}O_x, Ir_{0.2}Ru_{0.8}O_x, and RuO₂, (b) valence-state assignment of Ir, and (c) fitting curves in the radial distance (R-space) from the absorbing atom in FT-EXAFS.



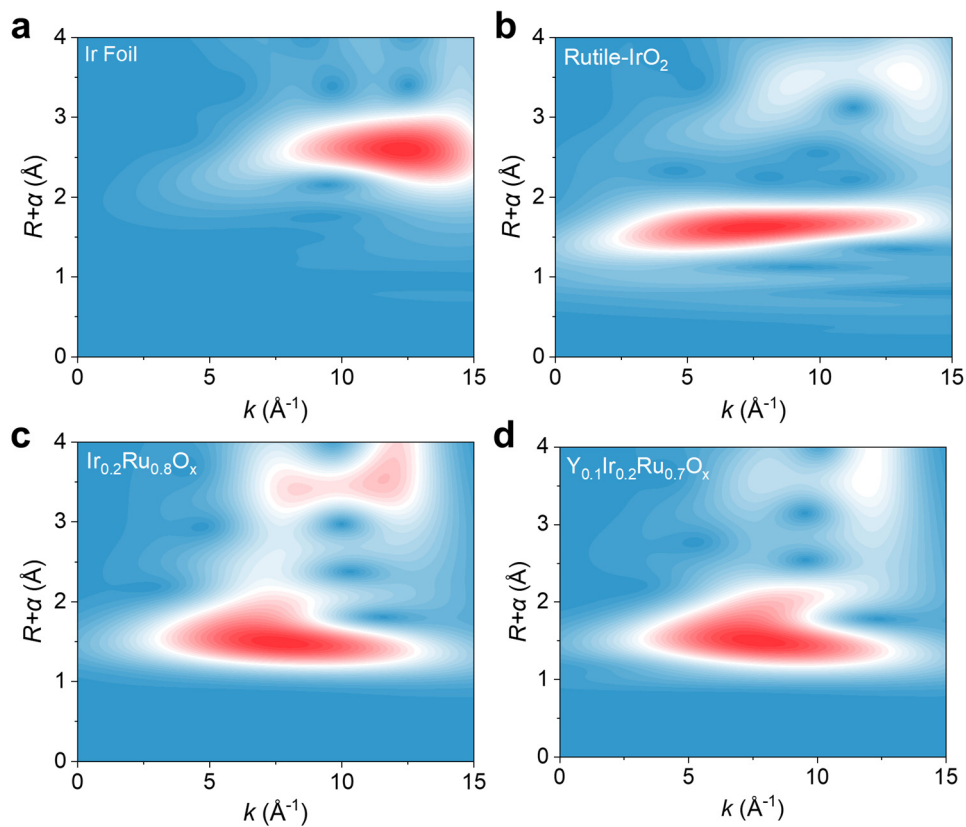
Supplementary Figure 36. Third order weighted (k^3 -weighted) fitted curves in (a) the weighted wavenumber space (k-space) and (b) the radial distance (R-space) from the absorbing atom for Ru Foil, Rutile-RuO₂, Ir_{0.2}Ru_{0.8}O_x, and Y_{0.1}Ir_{0.2}Ru_{0.7}O_x in FT-EXAFS.



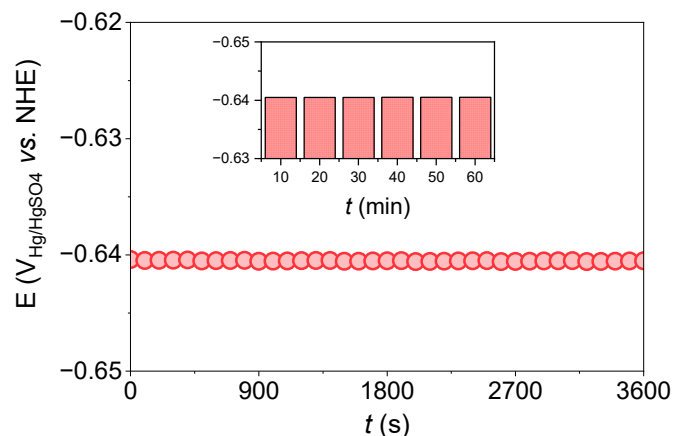
Supplementary Figure 37. Wavelet transform (WT) maps derived from third order weighted (k^3 -weighted) EXAFS spectra including the phase-corrected radial distance ($R+\alpha$) and the weighted wavenumber space (k -space) information for (a) Ru Foil, (b) Rutile-RuO₂, (c) Ir_{0.2}Ru_{0.8}O_x, and (d) Y_{0.1}Ir_{0.2}Ru_{0.7}O_x.



Supplementary Figure 38. Third order weighted (k^3 -weighted) fitted curves in (a) the weighted wavenumber space(k -space) and (b) the radial distance (R -space) from the absorbing atom for Ir Foil, Rutile-IrO₂, Ir_{0.2}Ru_{0.8}O_x, and Y_{0.1}Ir_{0.2}Ru_{0.7}O_x.

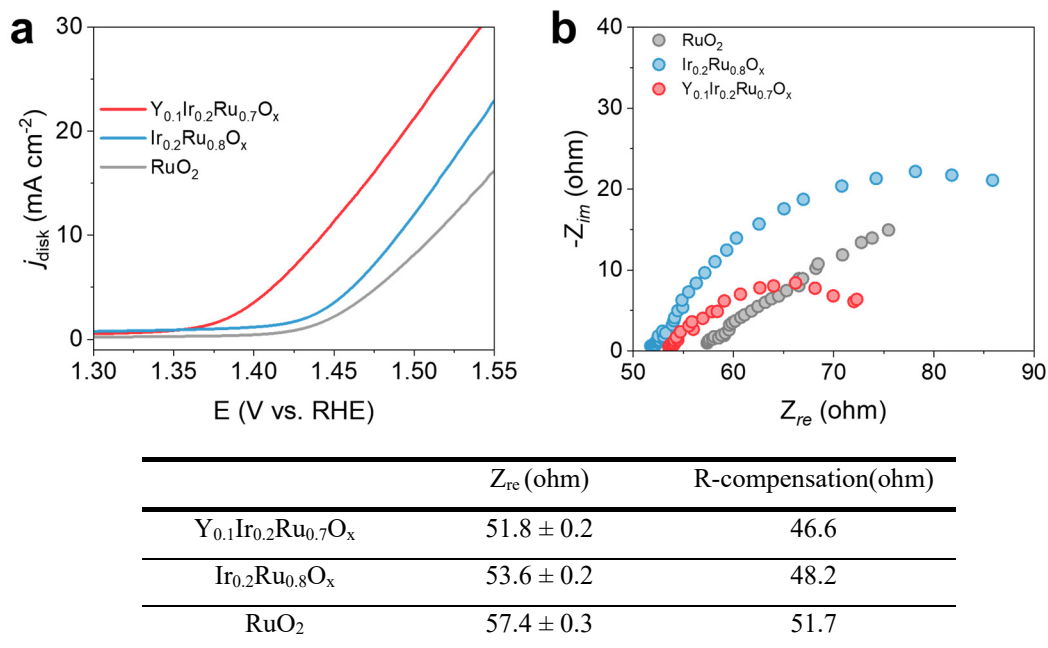


Supplementary Figure 39. Wavelet transform (WT) maps derived from third order weighted (k^3 -weighted) EXAFS spectra including the phase-corrected radial distance ($R+\alpha$) and the weighted wavenumber space (k -space) information for (a) Ir Foil, (b) Rutile-IrO₂, (c) Ir_{0.2}Ru_{0.8}O_x, and (d) Y_{0.1}Ir_{0.2}Ru_{0.7}O_x.

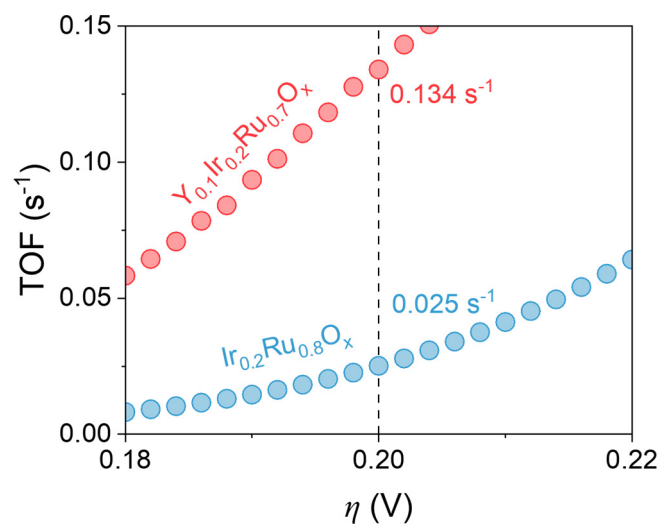


Supplementary Figure 40. Open-circuit potential curve over 3600 s in 0.1 M HClO₄ using a Hg/HgSO₄ reference electrode relative to NHE. Inset: Bar chart of the calibrated potential as a function of time (min).

To eliminate the influence of the reference electrode, the open-circuit potential of the Hg/HgSO₄ electrode in the electrolyte during the three-electrode test was calibrated against NHE. Under the given ionic strength, the solubility of hydrogen was assumed to remain constant regardless of pH. The reference electrode potential was maintained at 0.640 V vs. NHE at room temperature (~298 K).

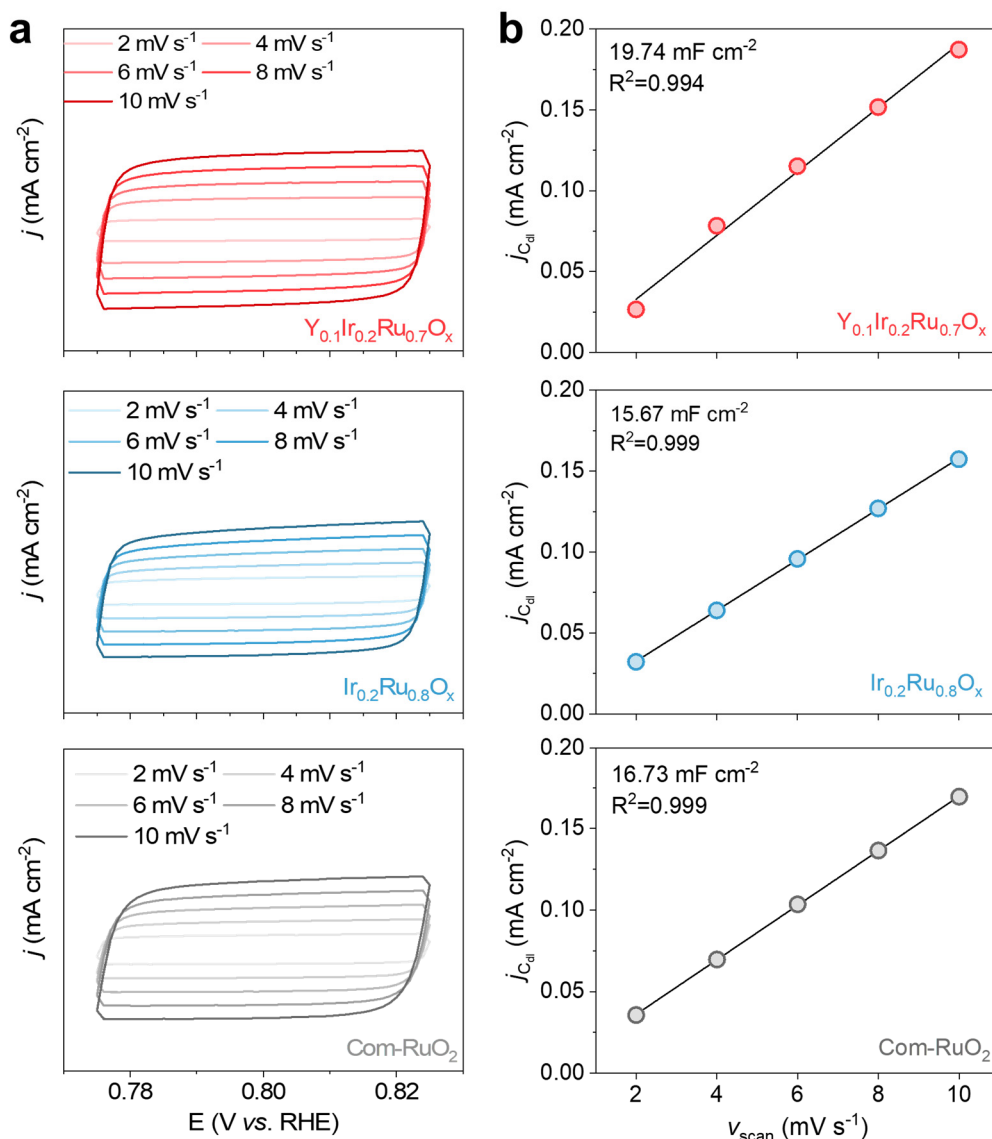


Supplementary Figure 41. (a) LSV curves without iR-compensation. (b) EIS Nyquist plots recorded for the iR correction of the LSV curves shown in Fig. 3a. Table: EIS real-axis impedance values and corresponding compensation values used for iR-compensation.



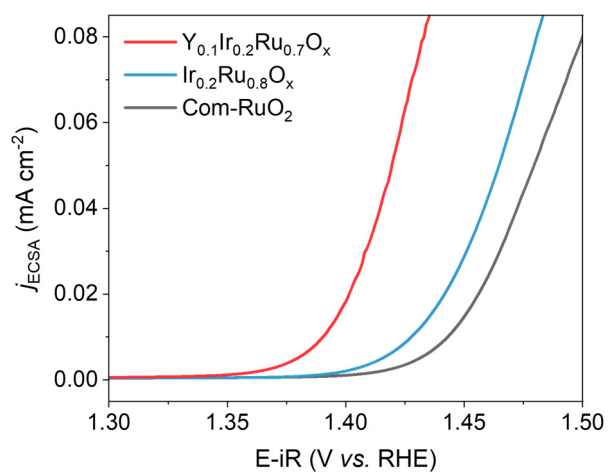
Supplementary Figure 42. The TOF values of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ and $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$ based on the ECSA.

Turnover Frequency (TOF) calculation are following these assumptions: (i) all surface planes are rutile- RuO_2 (110)²; (ii) The supplemented BET data (Supplementary Figure 27) were used as the source for the specific surface area values³; (iii) Faraday efficiency is considered to be 100%.

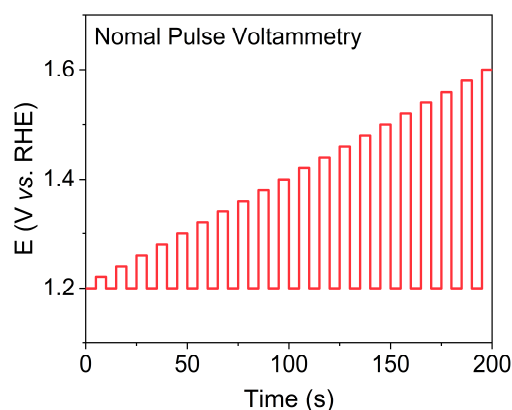


Supplementary Figure 43. (a) CV curves under different scan rates and (b) corresponding current density fitting curves for $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$, and Com-RuO_2 , respectively.

The ECSA was determined from the double-layer capacitance (C_{dl}) measured in the non-faradaic region. The cyclic voltammetry measurements were performed within the potential range of 0.775-0.825 V vs. RHE. The C_{dl} values were obtained from the slope of the current density (j_{cdl}) versus scan rate, and the ECSA was subsequently calculated according to $\text{ECSA} = C_{\text{dl}}/C_s$, where C_s was assumed to be 0.035 mF cm^{-2} .

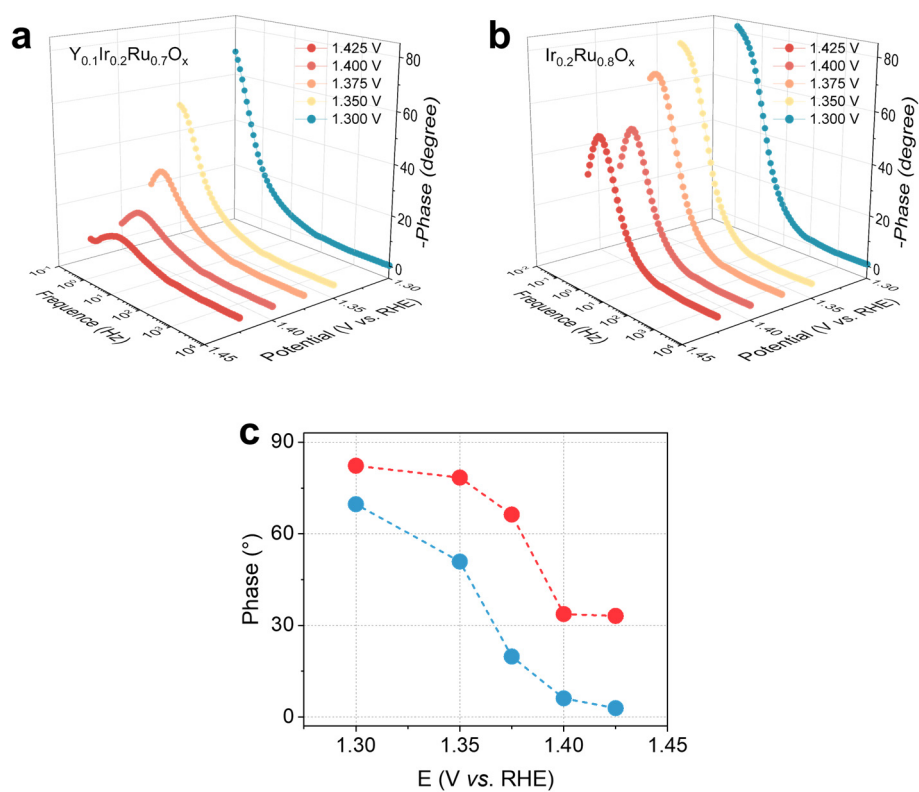


Supplementary Figure 44. LSV curves normalized by the ECSA for $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$, and Com- RuO_2 .

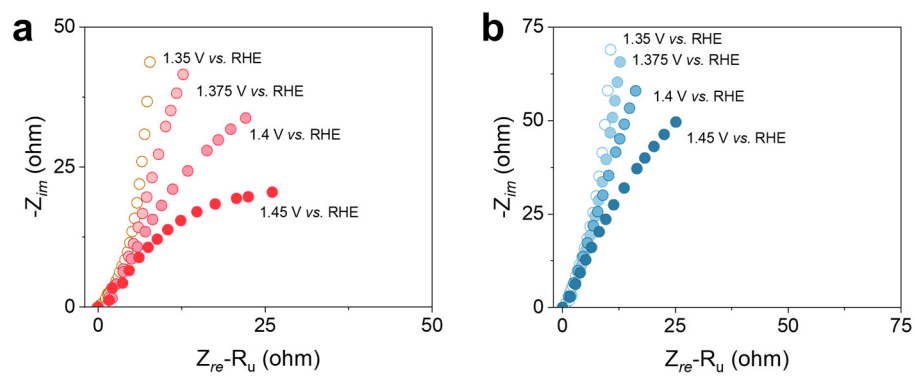


Supplementary Figure 45. Potential-time E-t curve acquired by pulse potentiostatic measurements.

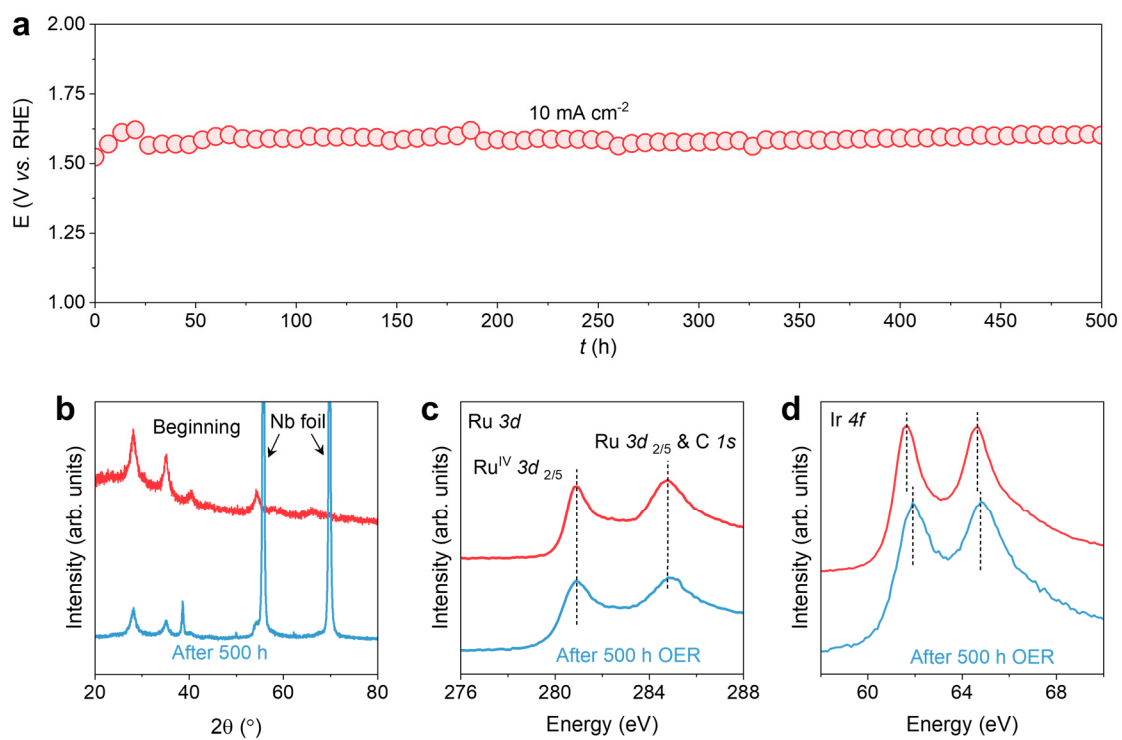
The adoption of a pulsed testing approach serves two primary purposes. First, it allows for a more accurate comparison of OER onset potentials among different catalysts in a three-electrode system, going beyond the conventional overpotential-based assessments. Second, the OER process can be conceptually interpreted as a cyclic accumulation and release of positive charge, resembling capacitive behaviour commonly referred to as pseudocapacitance or chemical capacitance. In this context, the distinction between pseudocapacitance and electrostatic double-layer (i.e., physical) capacitance provides a macroscopic probe into the underlying reaction kinetics and key mechanistic steps.



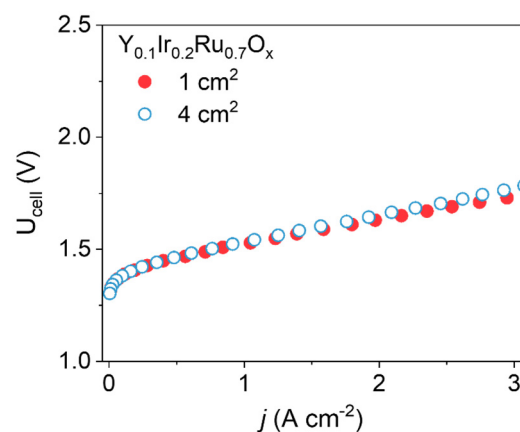
Supplementary Figure 46. Bode plots of AC impedance recorded at different potentials of (a) $Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$, (b) $Ir_{0.2}Ru_{0.8}O_x$, and (c) potential-phase comparison.



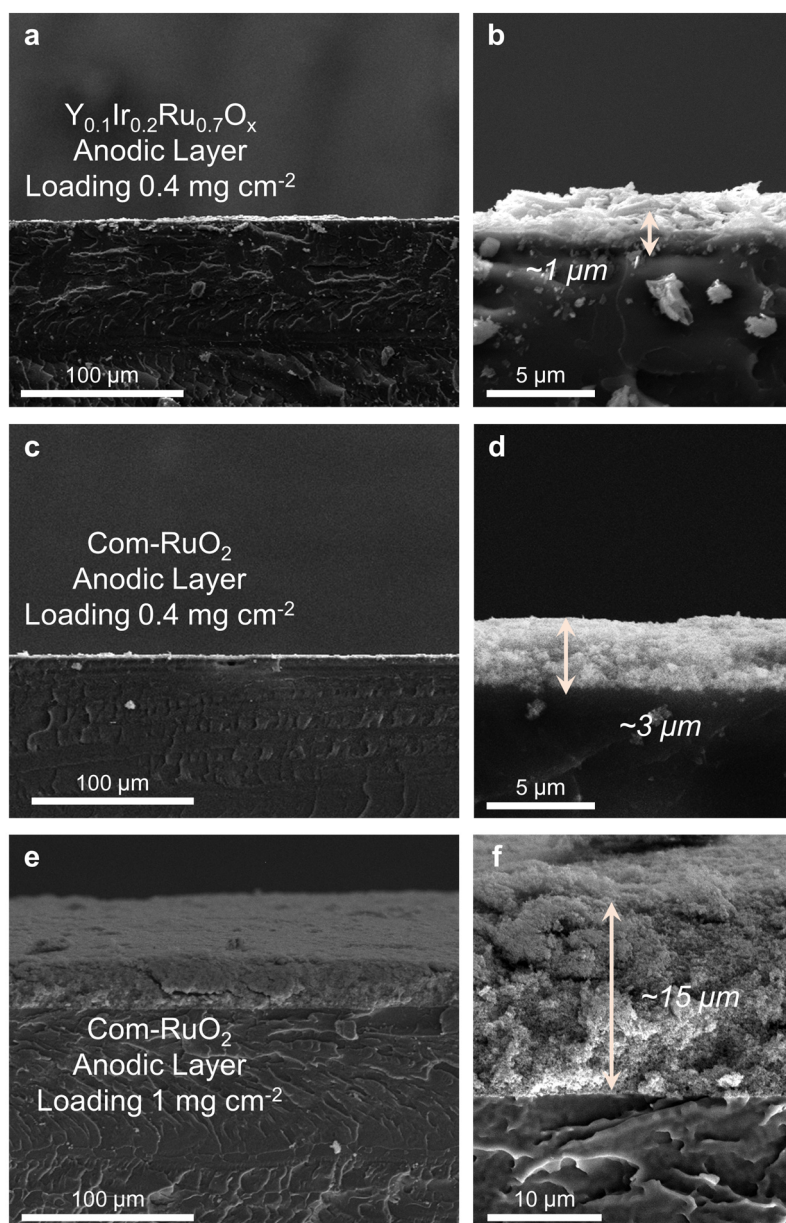
Supplementary Figure 47. Nyquist diagrams for (a) $Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$ and (b) $Ir_{0.2}Ru_{0.8}O_x$.



Supplementary Figure 48. (a) E-t curve at 10 mA cm^{-2} over 500 h of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$. Comparisons of (b) XRD patterns and (c, d) Ru 3d/Ir 4f XPS spectra of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ before and after testing.

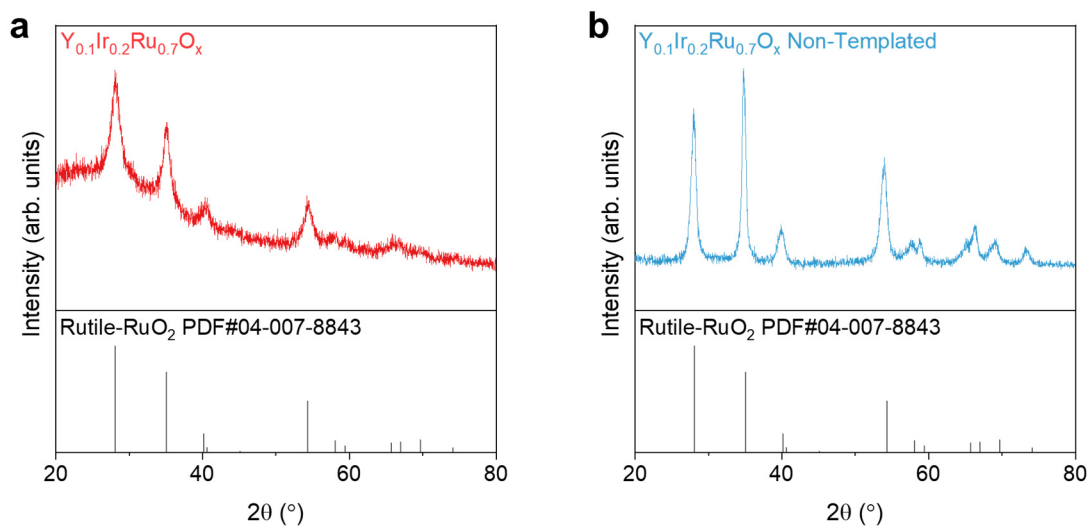


Supplementary Figure 49. U_{cell}-current density curves of PEMWE devices assembled with MEAs of different geometric areas using Y_{0.1}Ir_{0.2}Ru_{0.7}O_x as the anodic catalyst. Comparable performance was observed for Y_{0.1}Ir_{0.2}Ru_{0.7}O_x samples with different surface areas, indicating negligible size-dependent effects.



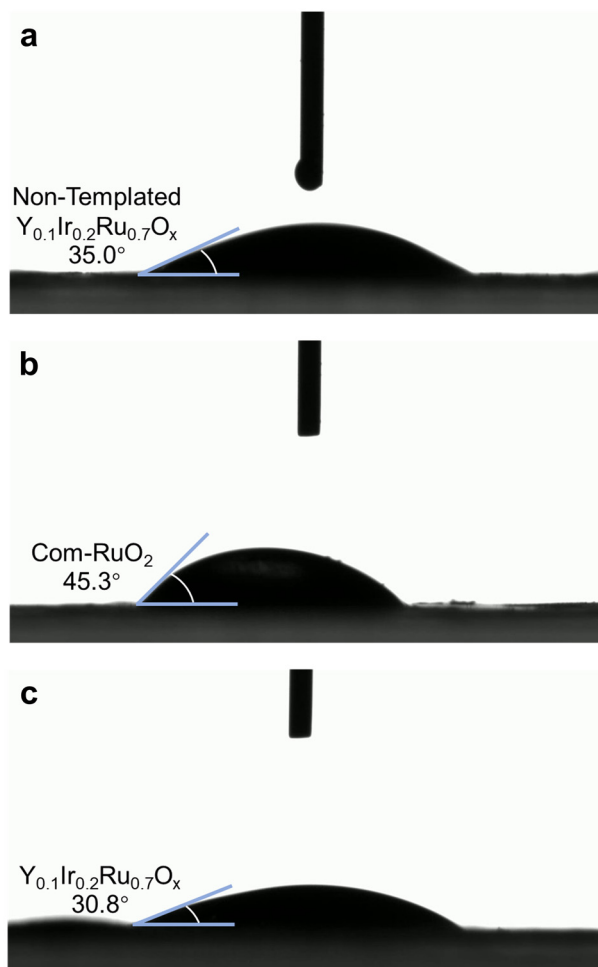
Supplementary Figure 50. Cross-sectional MEA interface images loaded with (a, b) 0.4 mg cm^{-2} $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, (c, d) 0.4 mg cm^{-2} Com-RuO₂, and (e, f) 1.0 mg cm^{-2} Com-RuO₂ together with their corresponding magnified SEM micrographs.

The cross-sectional thickness of the MEA was examined by freeze-fracture method⁴. As the nanosheet lamellar structure of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, its catalyst layer is much thinner than that of commercial RuO₂ at the same loading. In contrast, at typical industrial-grade loadings, particulate commercial RuO₂ tends to undergo particle agglomeration and pore enlargement, resulting in a loose catalyst layer that thickens to approximately 15 μm . This enabled the use of a significantly thin anode catalyst layer, thereby substantially reducing precious metal consumption.



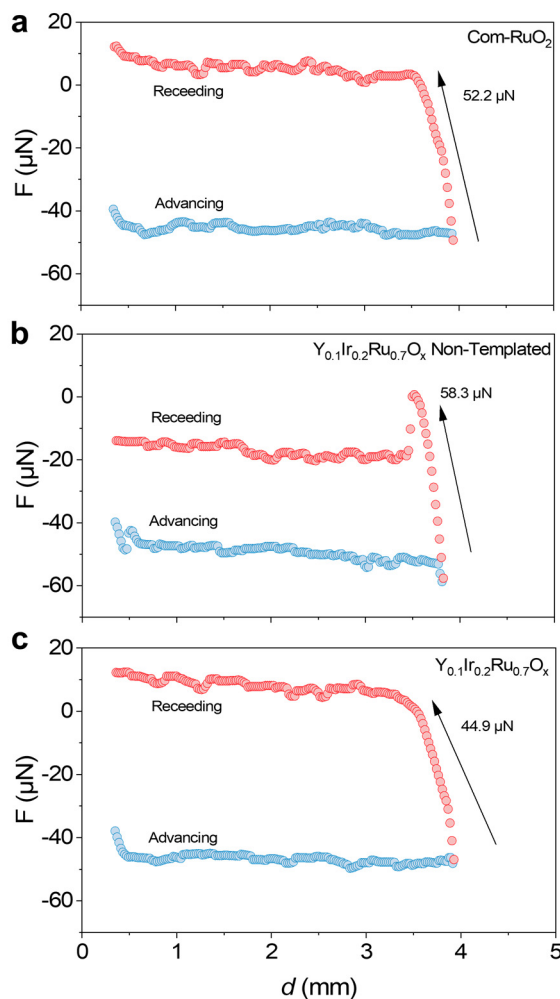
Supplementary Figure 51. Comparison of XRD patterns for (a) $Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$ and (b) $Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$ without template obtained from different synthesis methods.

$Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$ non-templated refers to a control sample synthesized via sol-gel co-precipitation followed by annealing, in which the metal precursor ratios are kept identical to those of the primary sample $Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$.



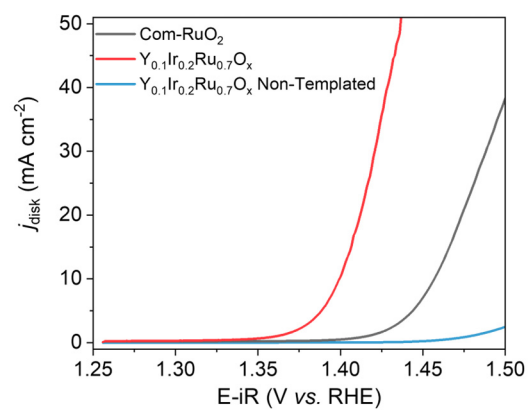
Supplementary Figure 52. The first-frame images from the contact angle measurement for using deionized water as the probing medium. (a) Com-RuO₂, (b) Y_{0.1}Ir_{0.2}Ru_{0.7}O_x non-templated, and (c) Y_{0.1}Ir_{0.2}Ru_{0.7}O_x.

For comparison, a non-templated Y_{0.1}Ir_{0.2}Ru_{0.7}O_x sample was prepared via co-precipitation of metal salts in a water bath, aiming to assess the intrinsic physical property differences arising from distinct synthesis strategies, in contrast to the sacrificial template method. The contact angle measurements primarily reflect differences in hydrophilicity among the three samples. Given that the OER occurs at the catalyst-electrolyte interface and involves liquid-phase contact, catalysts with intrinsically hydrophilicity ensure the enhanced adsorption behaviour during the reaction process.

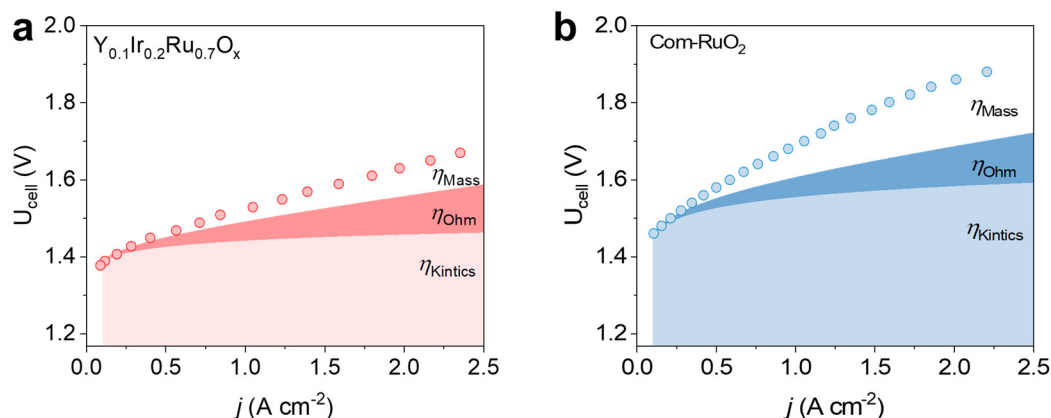


Supplementary Figure 53. Stretching force (F)-operating distance (d) curves of bubble (air) adhesion measurements in aqueous solution on the catalyst layer of the MEAs for (a) Com-RuO₂, (b) Y_{0.1}Ir_{0.2}Ru_{0.7}O_x non-templated, and (c) Y_{0.1}Ir_{0.2}Ru_{0.7}O_x.

Due to the strong hydrophilicity of the primary sample, conventional pellet pressing was not suitable for direct measurement. Instead, the bubble adhesion force test was conducted on catalyst layers spray-coated onto pre-soaked Nafion 115 membranes. Complementary to the previous water contact angle test, this measurement reflects the interfacial force behaviour during gas bubble detachment from the catalyst surface. From Supplementary Figure 49, the primary Y_{0.1}Ir_{0.2}Ru_{0.7}O_x sample exhibited significantly lower bubble adhesion, whereas the reliance free Y_{0.1}Ir_{0.2}Ru_{0.7}O_x synthesized via the alternative co-precipitation route showed pronounced bubble retention. This difference is attributed to the interconnected mesoporous structure of the template-derived Y_{0.1}Ir_{0.2}Ru_{0.7}O_x, which facilitates gas release under high current density and thereby reduces mass transport overpotential.

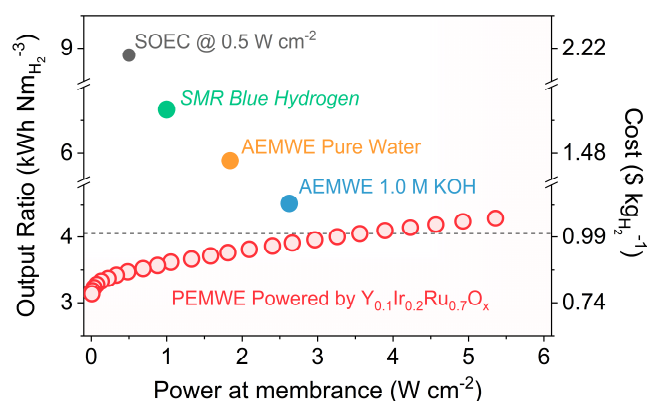


Supplementary Figure 54. LSV curves obtained of Com-RuO₂, Y_{0.1}Ir_{0.2}Ru_{0.7}O_x, and Y_{0.1}Ir_{0.2}Ru_{0.7}O_x non-templated from different synthesis methods.



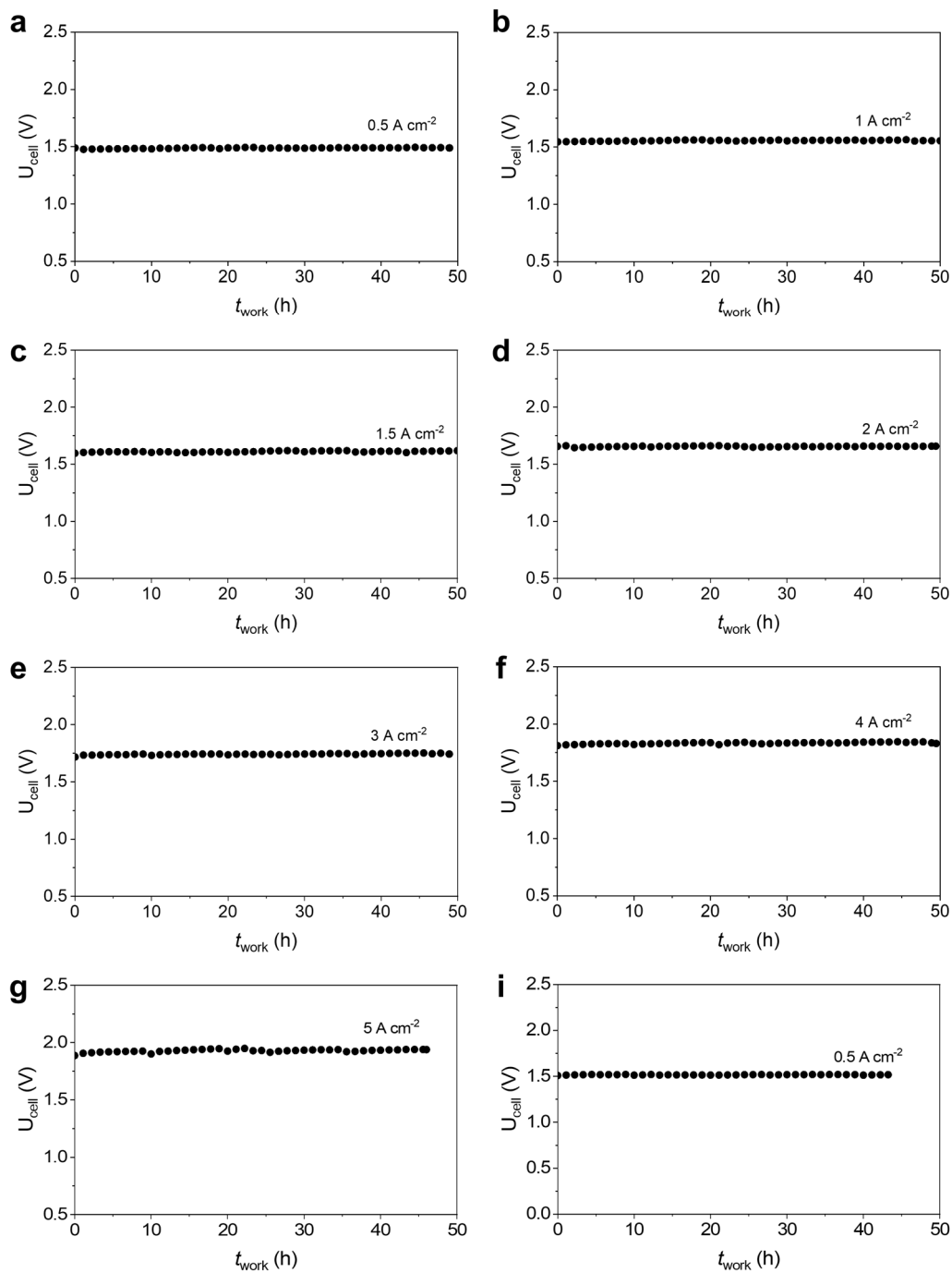
Supplementary Figure 55. Deconvolution of the total overpotential into kinetic, ohmic, and mass transport components for (a) $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ and (b) Com-RuO_2 .

The overpotential was deconvoluted into three components: kinetic overpotential (including intrinsic voltage and kinetic loss), ohmic overpotential, and mass transport overpotential. The kinetic overpotential is derived by fitting the derivative of voltage with respect to current density in the low-current region to a $U\text{-Log } j$ relationship. The ohmic overpotential is directly determined from the measured high-frequency resistance, taken as the reaction resistance (A: 55 m Ω ; B: 50 m Ω). The remaining portion of the total overpotential was attributed to mass transport limitation.

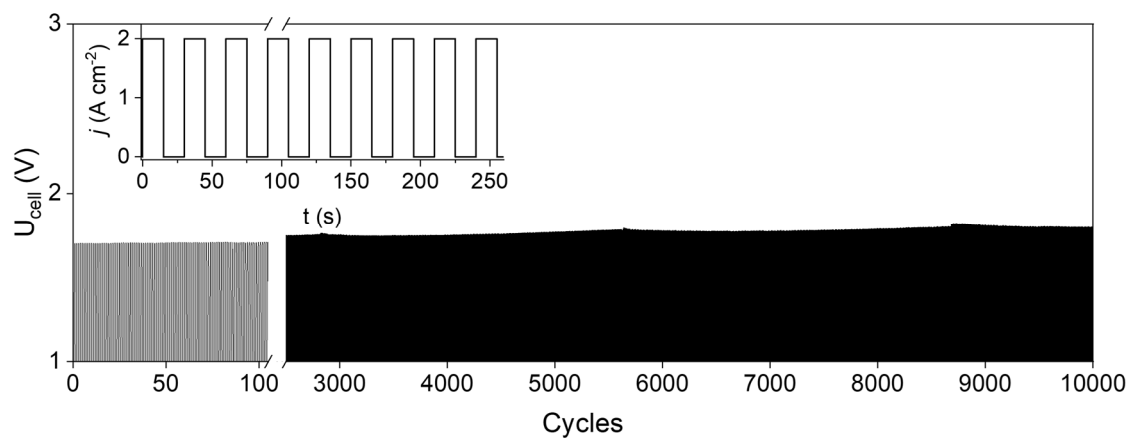


Supplementary Figure 56. The comparison of output ratio, hydrogen production cost, and membrane power (unit power) among typical hydrogen production methods, including the PEMWE device assembled with $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ as the anodic catalyst.

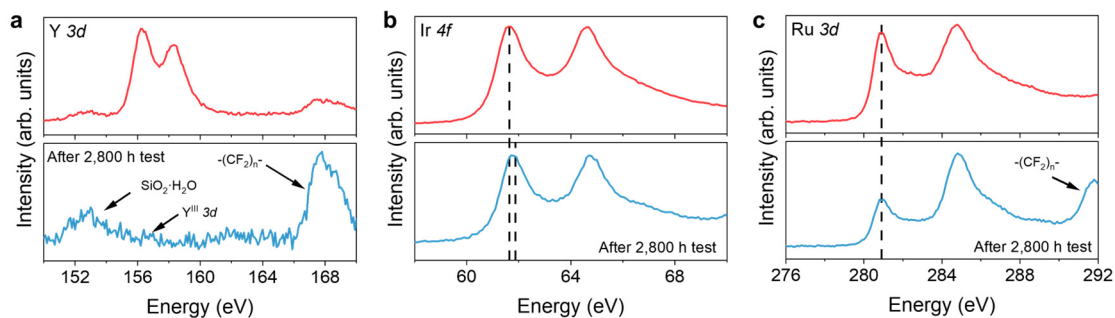
The hydrogen production electricity price is calculated at $0.022 \text{ \$ kWh}^{-1}$, with long-term losses and MEA installation costs included. According to DOE data, solid oxide electrolysis cell (SOEC) operates at 0.5 W cm^{-2} , steam methane reforming (SMR) blue hydrogen costs $1.5 \text{ \$ kg}^{-1}$, and AEMWE operates at $1.87 \text{ V @ } 1 \text{ A cm}^{-2}$ (pure water) and $1.75 \text{ V @ } 1.5 \text{ A cm}^{-2}$ (1 M KOH electrolyte).



Supplementary Figure 57. U_{cell} - t curves recorded during the stepped-current PEMWE test, operated sequentially at (a to g) 0.5 - 5 A cm^{-2} and finally back to (i) 0.5 A cm^{-2} .

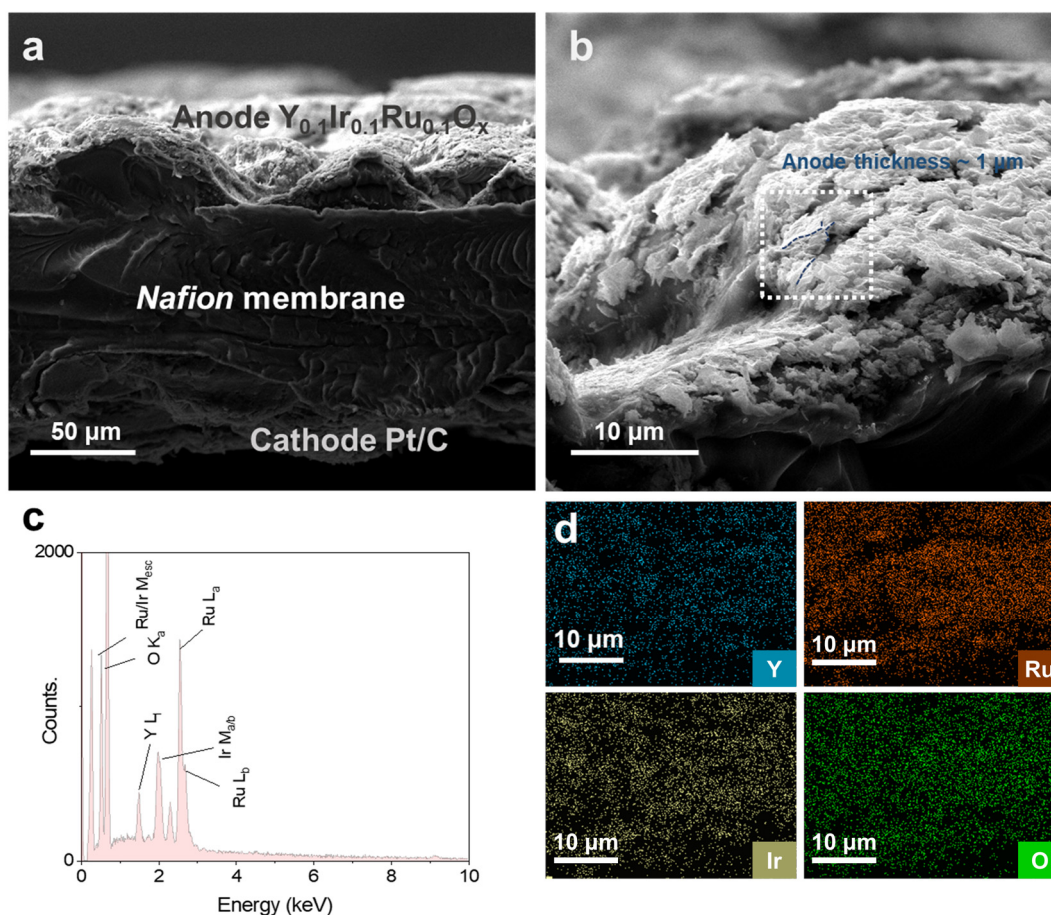


Supplementary Figure 58. U_{cell} -cycle profile of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ under square-wave ADT operation. Inset: Applied square-wave ADT waveform.

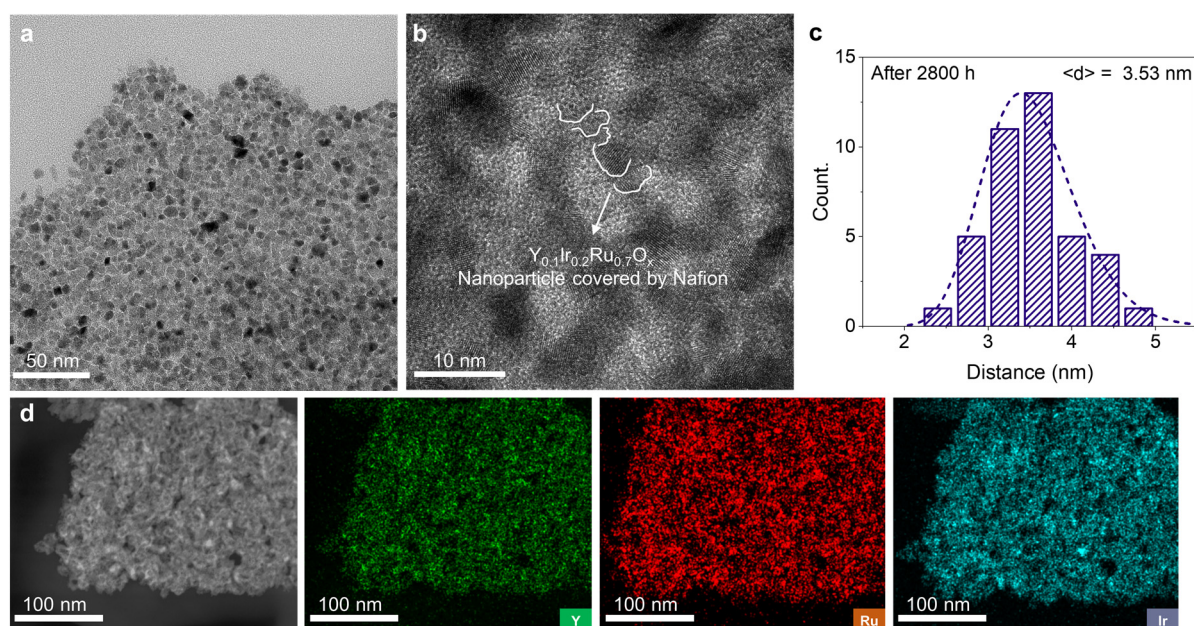


Supplementary Figure 59. XPS spectra of (a) Y 3d, (b) Ru 3d, and (c) Ir 4f in $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ recorded before and after 2800 h @ 3 A cm^{-2} of continuous operation in PEMWE.

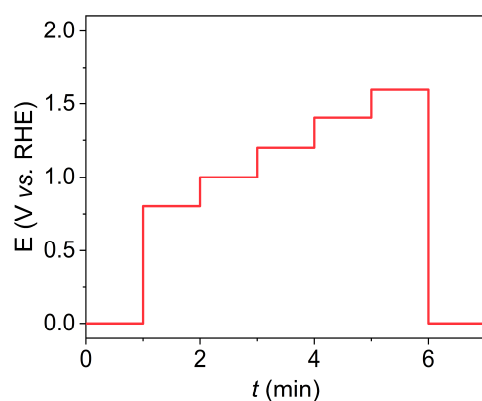
Post-test analysis revealed substantial residues of silica from the electrolyser gasket and sulfonate groups from residual Nafion on the catalyst surface. The XPS signals of both species overlapped with Y 3d and obscured the intrinsic Y 3d signal due to their high abundance. Furthermore, ICP-MS tracking measurements (Supplementary Table 7) indicated negligible Y leaching.



Supplementary Figure 60. SEM images of the MEA after 2800 h of operation. (a) Cross-sectional SEM image of the entire MEA. (b) Enlarged view of the anode layer. Dashed box: Anode catalyst deposited on the Nafion membrane. (c) EDS data obtained by SEM-EDS. (d) SEM-EDS mappings of Y, Ir, Ru, and O.

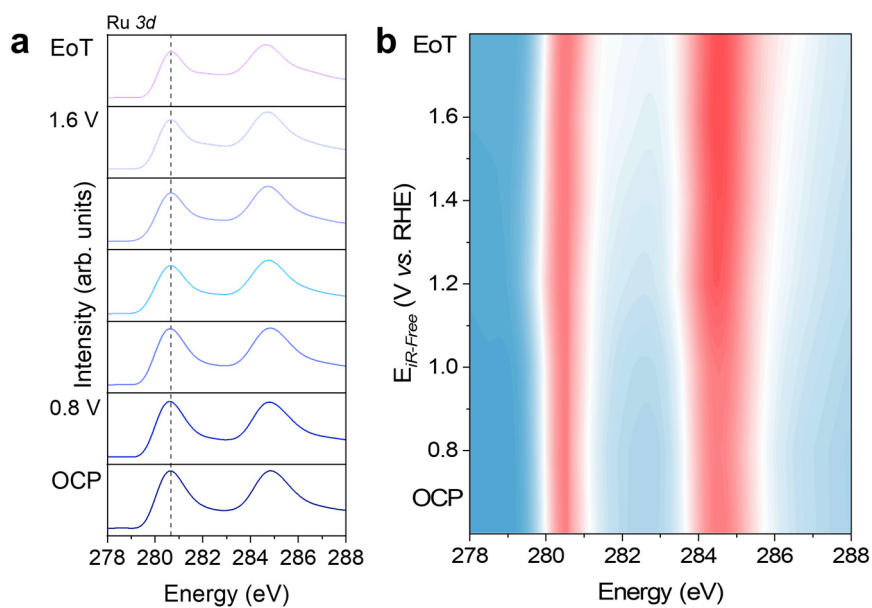


Supplementary Figure 61. HR-TEM characterization of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ on the MEA after 2800 h of operation. (a) Single-layer $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ after reaction. (b) Enlarged view of locally interconnected particles. Dashed outline: Shadow of an individual $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ nanoparticle. (c) Particle-size distribution of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ after reaction. (d) EDS mappings for the elemental distribution.



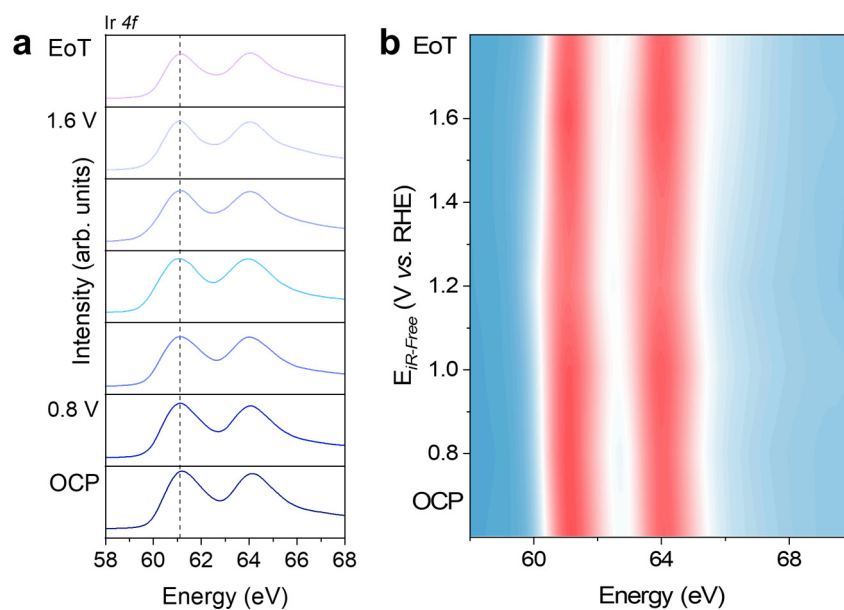
Supplementary Figure 62. E-t curves recorded during *in-situ* XPS measurements.

Since *in-situ* XPS does not capture spectra under continuously applied bias, the observed shift in a single XPS peak is generally interpreted as the change in elemental oxidation state after the application of potential.

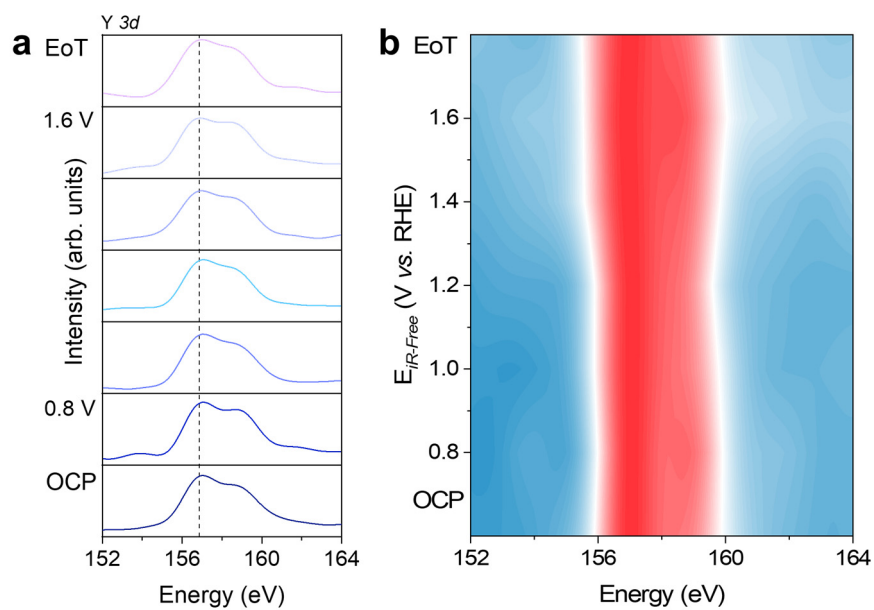


Supplementary Figure 63. (a) *Quasi-in situ* XPS spectra of Ru 3d in $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ and (b) the corresponding peak position surface distribution map.

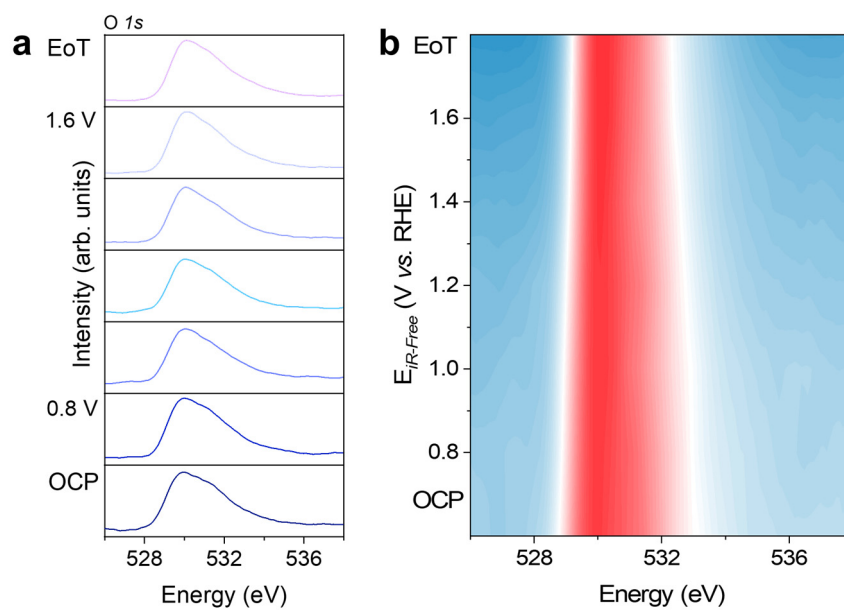
Tests were conducted in the potential range of 0.8-1.6 V vs. RHE to investigate the relationship between the oxidation state changes of the catalyst samples and the transition from the pre-adsorption stage to the more complete OER process.



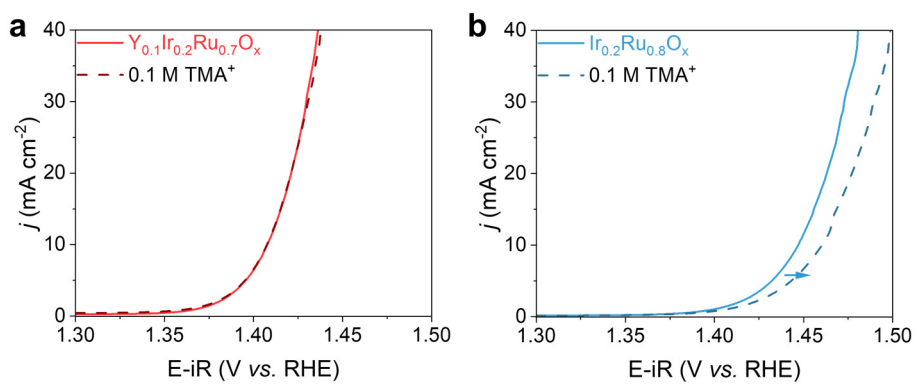
Supplementary Figure 64. (a) *Quasi-in situ* XPS spectra of Ir 4f in $Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$ and (b) the corresponding peak position surface distribution map.



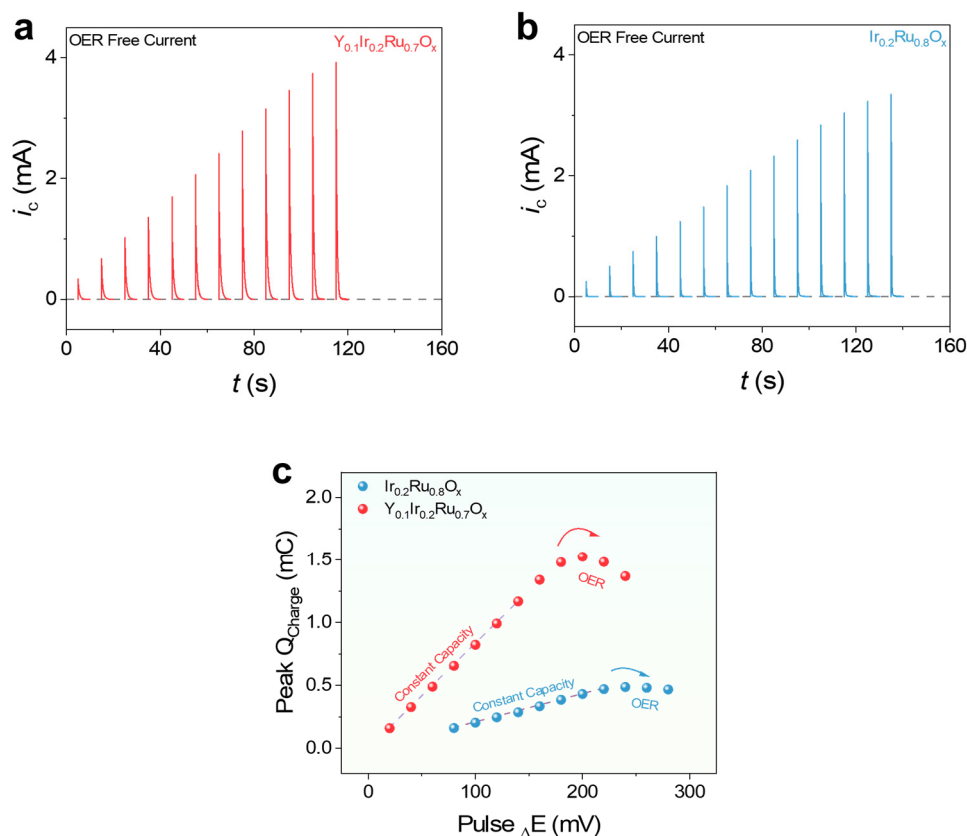
Supplementary Figure 65. (a) *Quasi-in situ* XPS spectra of Y 3d in $Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$ and (b) the corresponding peak position surface distribution map.



Supplementary Figure 66. (a) *Quasi-in situ* XPS spectra of O *1s* in $Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$ and (b) the corresponding peak position surface distribution map.

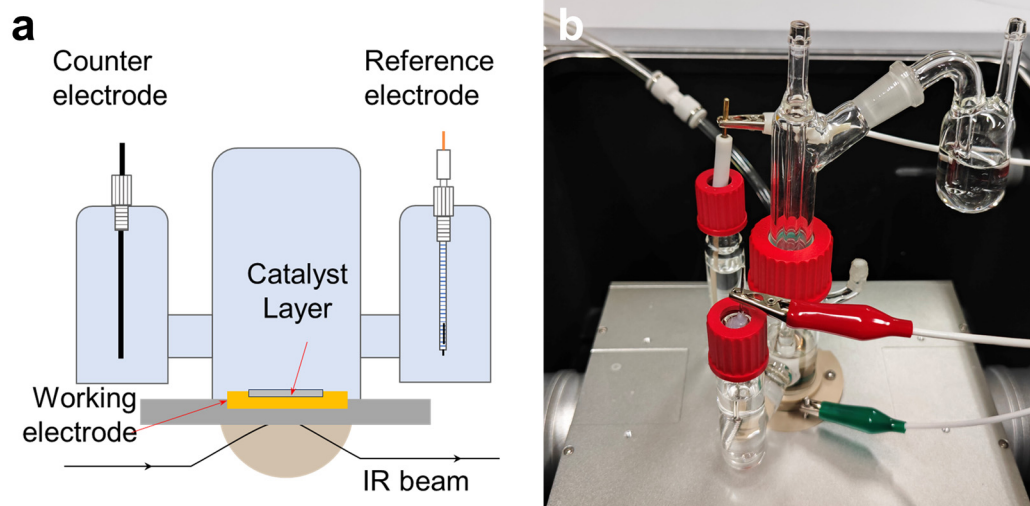


Supplementary Figure 67. Comparison of the LSV curves of (a) $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ and (b) $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$ before and after TMA^+ poisoning.

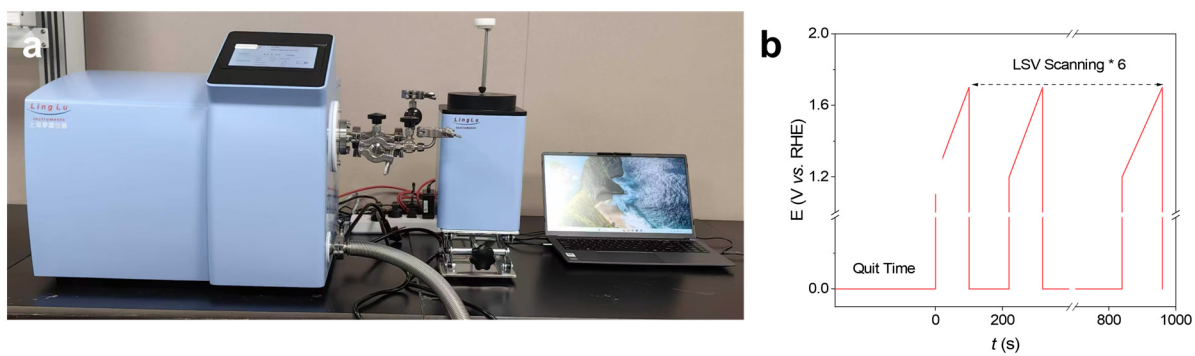


Supplementary Figure 68. Integral areas of OER Faradaic current removal during NPV testing for (a) $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, (b) $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$, and (c) integral results.

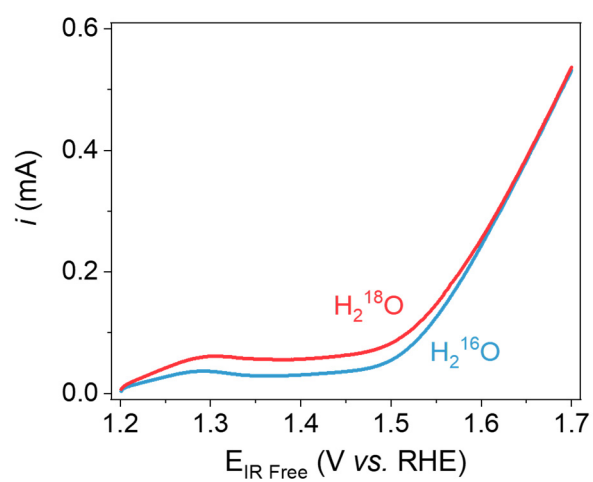
The difference in pseudocapacitance between $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ and $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$ ($118.60 \text{ mF cm}^{-2}$ and 31.72 mF cm^{-2}) is substantially greater than that in their double-layer capacitance, providing direct evidence that $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ and $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$ follow fundamentally different reaction pathways.



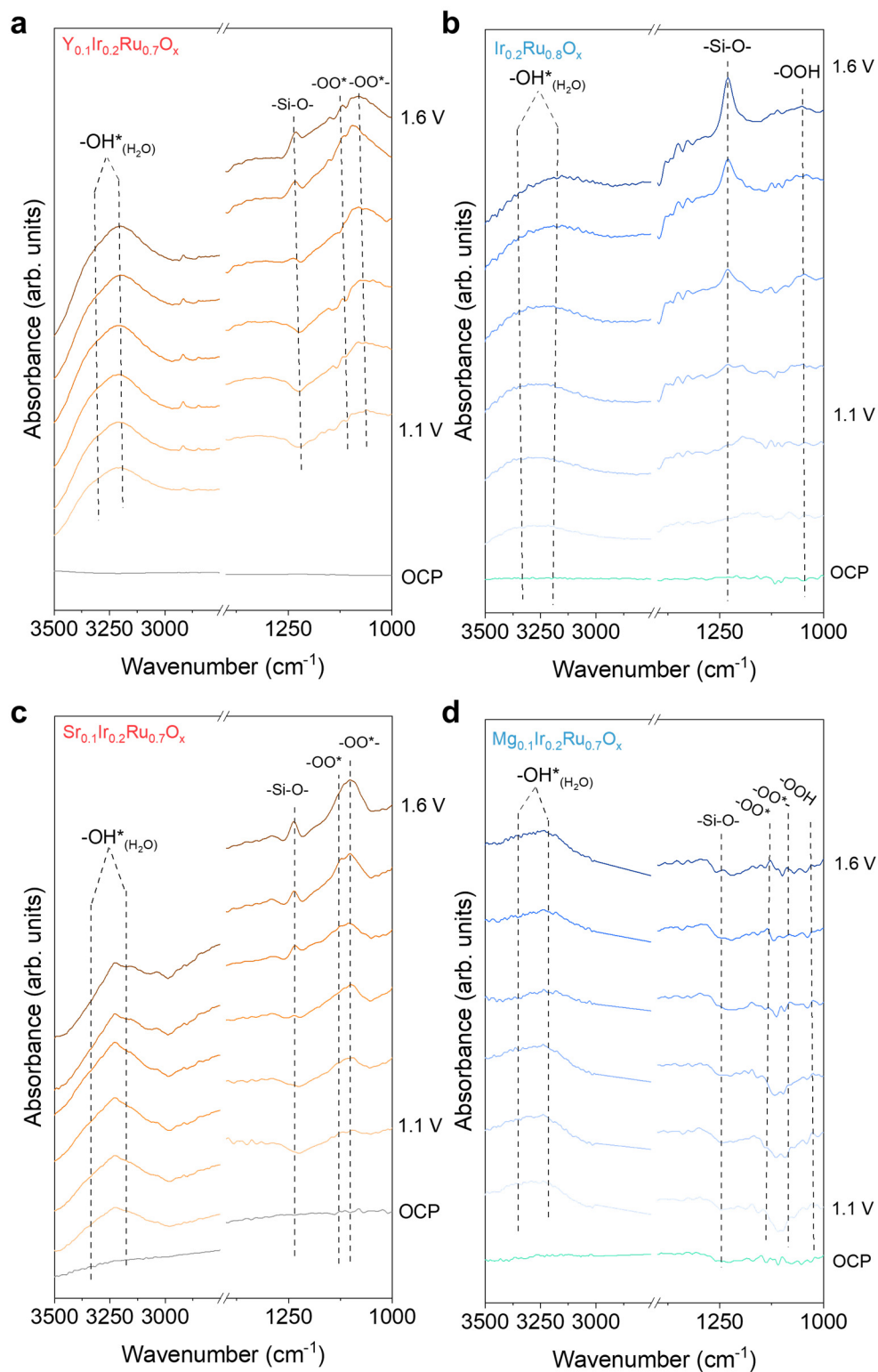
Supplementary Figure 69. (a) Schematic diagram and (b) corresponding photograph of ATR-FTIRAS setup.



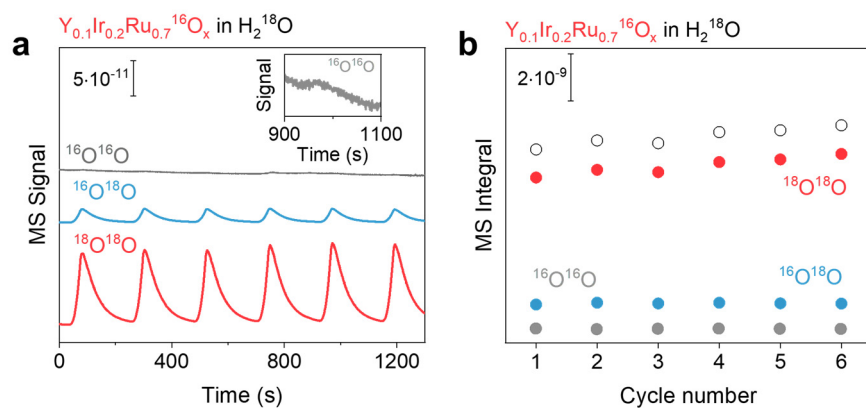
Supplementary Figure 70. (a) Photograph of the DEMS setup. (b) Potential-time profile recorded during the DEMS measurement.



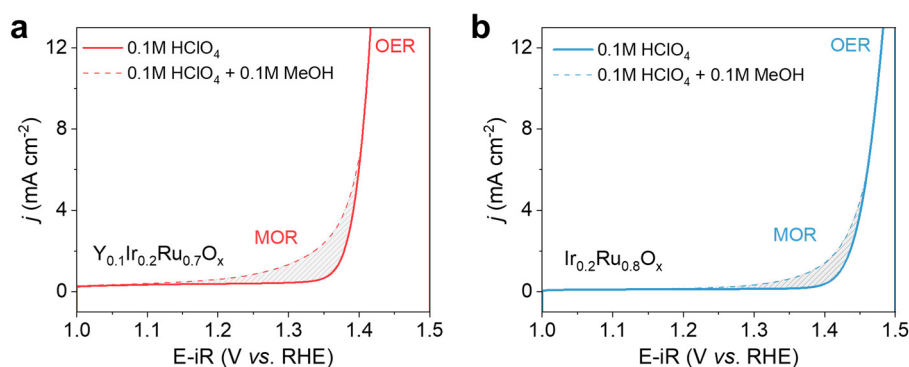
Supplementary Figure 71. Comparison of LSV curves of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ during DEMS test in H_2^{18}O and H_2^{16}O environments.



Supplementary Figure 72. ATR-FTIR spectra for (a) $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, (b) $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$, (c) $\text{Sr}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, and (d) $\text{Mg}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$. The testing process has been provided in the method section. The shift in peak position is induced by changes in surface coverage.

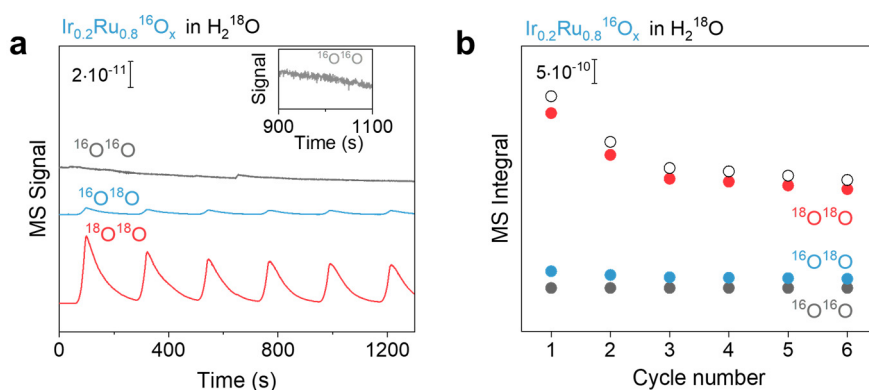


Supplementary Figure 73. (a) MS signal-time curves for $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ in H_2^{18}O . Inset: single peak position signal amplification of MS for $^{36}\text{O}_2$. (b) the corresponding species integral intensity graph.



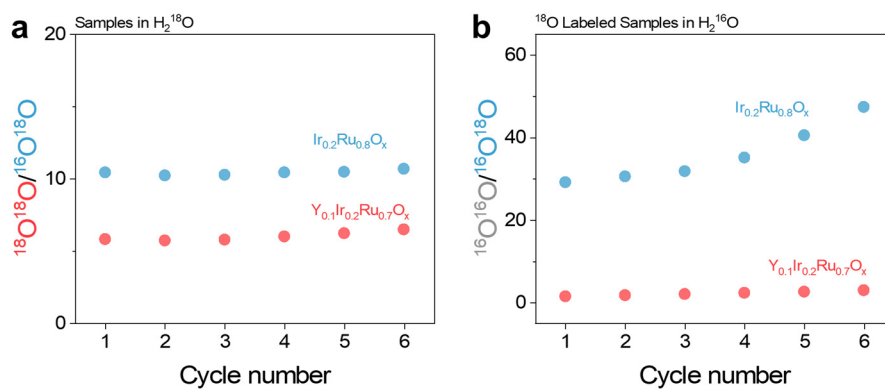
Supplementary Figure 74. Comparison of LSV curves for OER and MOR on (a) $Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$ and (b) $Ir_{0.2}Ru_{0.8}O_x$ with area differences marked.

After normal OER testing, pure methanol was added to 0.1 M $HClO_4$ electrolyte to achieve a final concentration of 0.1 M. CV scanning was conducted from 1 - 1.4 V vs. RHE until stabilization, followed by LSV testing. LSV curves for methanol oxidation reaction (MOR) were compared with normal OER results to quantify $*OH$ adsorption.

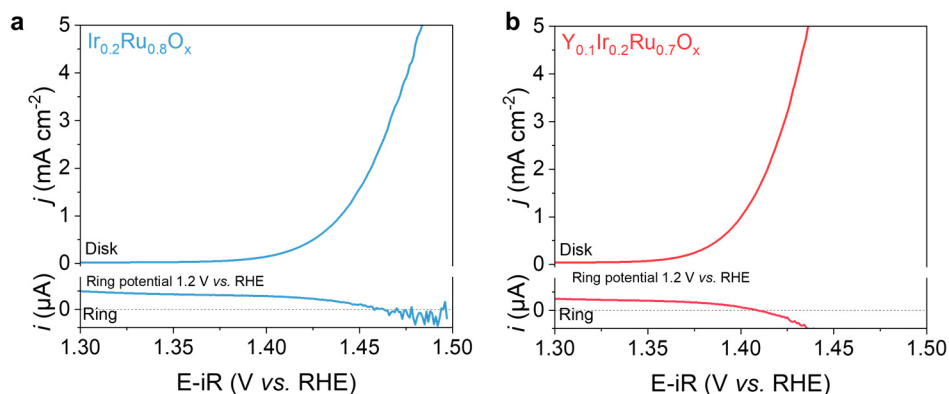


Supplementary Figure 75. (a) MS signal-time curves of $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$ in H_2^{18}O . Inset: single peak position signal amplification of MS for $^{36}\text{O}_2$. (b) the corresponding species integral intensity graph.

Due to the unavoidable presence of atmospheric $^{32}\text{O}_2$ in the reaction chamber⁵, the signal-to-noise ratio for $^{32}\text{O}_2$ was suboptimal in the initial test aimed at labelling the catalyst surface with ^{18}O . As a result, the data from this stage could only provide a general indication of whether the catalyst followed the OPM, without enabling a definitive assessment of pathway selectivity. In the case of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$, a weak $^{32}\text{O}_2$ signal with noticeable noise was consistently detected at the expected mass spectrometric elution times in each cycle, whereas no corresponding signal was observed for the $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$ sample under identical condition. This observation provides additional support for the presence of OPM-active sites in $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$.

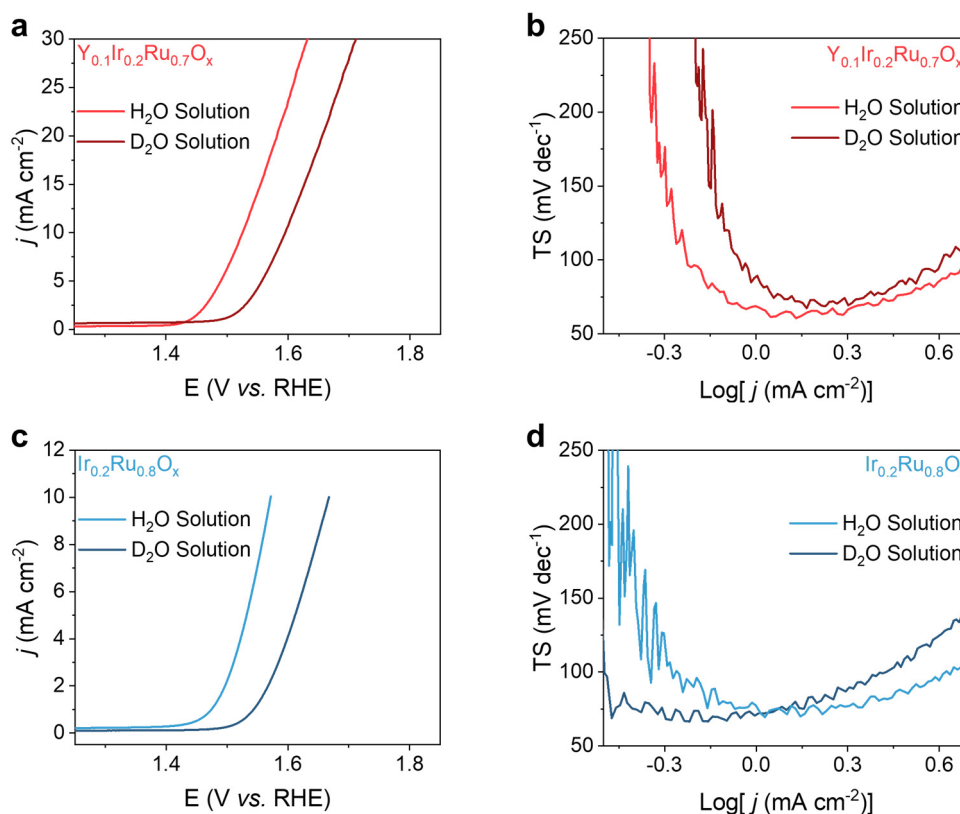


Supplementary Figure 76. Comparison of $^{36}\text{O}_2/^{34}\text{O}_2$ and $^{32}\text{O}_2/^{34}\text{O}_2$ integral intensities of $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$ and $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ in (a) H_2^{18}O and (b) H_2^{16}O environments.



Supplementary Figure 77. Comparison of ring and disk electrode currents during the LSV measurements for (a) $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$ and (b) $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$. The scan rate was set to 2 mV s^{-1} , scanning from the low-potential region toward higher potentials,

The ring and disk currents near the onset potential were recorded, and the ring electrode was operated at a fixed potential of 1.2 V vs. RHE to capture -OOH-derived byproducts formed via bypass pathways⁶.



Supplementary Figure 78. (a) LSV curves of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ measured in H_2O and D_2O , and (b) corresponding TS- $\log j$ plots. (c) LSV curves of $\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$ measured in H_2O and D_2O , and (d) corresponding TS- $\log j$ plots.

Due to the surface passivation of Nb and the slower bubble-dispersion dynamics in the absence of external hydrodynamic assistance, the LSV curves collected on Nb foil generally appear not as smooth as those on RDE.

Supplementary Table 1. Comparison of the performance of various OER catalysts under 3-electrode and PEMWE conditions.

No.	Catalyst.	3-Electrode Performance		PEMWE Performance				Ref.
		η_{10} (mV)	Tafel Slope (mV dec ⁻¹)	Testing Conditions	Anode Loading (mg cm ⁻²)	U _{cell} @ 3A cm ⁻² (V)	Stability (h)	
1	Y _{0.1} Ir _{0.2} Ru _{0.7} O _x	170	38.7	N115 80°C	0.4 _{PGM} (0.1 Ir)	1.75	2800 @ 3 A cm ⁻²	This Work
2	Ir _{0.2} Ru _{0.8} O _x	210	54		0.4 _{PGM} (0.1 Ir)	2.03	300 @ 1 A cm ⁻²	
3	Com-RuO ₂	233	61		0.8 _{PGM}	1.90 @ 2.6 A cm ⁻²	5* @ 1 A cm ⁻²	This Work
4	IrO _x ·nH ₂ O	283	47	N115 60°C	2 Ir	2 @ 2 A cm ⁻²	600 @ 1 A cm ⁻²	
5	Nb _{0.1} Ru _{0.9} O _x	203	43.8	N117 80°C	2 _{cat.}	2.1	100 @ 0.3 A cm ⁻²	8
6	ZnRuO _x	255	50	/	2 _{cat.}	2.0	120 @ 0.2 A cm ⁻²	9
7	IrRu HNWs	215	59	N115	0.35 Ir	1.9	240 @ 2 A cm ⁻²	10
8	HEA@Ir-MEO	245	56.2	N212 60°C	0.8 _{PGM} (0.4 Ir)	1.85	500 @ 1 A cm ⁻²	11
9	SrIr _{0.2} Ru _{0.8} O _x	180	39	N212 60°C	2 _{cat.}	1.60 @ 2 A cm ⁻²	150 @ 1 A cm ⁻²	12
10	TS-Ir/MnO ₂	198	56.6	N117 60°C 0.1 M HClO ₄	1 _{cat.}	/	200 @ 0.5 A cm ⁻²	13
11	Ru/Ti ₄ O ₇	150	43.81	N117 60°C	0.4 _{PGM}	1.95 @ 2 A cm ⁻²	300 @ 0.5 A cm ⁻²	14
12	Ba _{0.3} (SO ₄) _δ W _{0.2} Ru _{0.5} O _{2-δ}	206	43.3	N115 80°C 0.5 M H ₂ SO ₄	3 _{cat.}	2.1	300 @ 1 A cm ⁻²	15
13	Ru _{0.5} Ir _{0.5} O ₂	151	45	N117 25°C	0.8 _{PGM} (0.5 Ir)	1.82 @ 2 A cm ⁻²	200 @ 0.25 A cm ⁻²	16
14	IrO _x /TiN	293	40.8	N212 60°C 0.1 M HClO ₄	0.2 Ir	1.69 @ 1 A cm ⁻²	40 @ 0.1 A cm ⁻²	17
15	Ir/Nb ₂ O _{5-x}	218	52.3	N115 80°C	3 _{cat.}	1.839	2000 @ 2 A cm ⁻²	18
16	Ru array-Co ₃ O ₄	160	16	/	/	1.80 @ 2 A cm ⁻²	100 @ 1 A cm ⁻²	19
17	IrB _{1.1}	248	58	N115 80°C	2 _{cat.}	2.15 @ 2 A cm ⁻²	100 @ 0.5 A cm ⁻²	20

18	Ta _{0.1} Tm _{0.1} Ir _{0.8} O _{2-δ}	198	64.0	50°C 0.5 M H ₂ SO ₄	0.2 Ir	1.935	500 @ 1.5 A cm ⁻²	21
19	IrO ₂ @TaO _x @TaB	276	/	N115 80°C	0.6 Ir	1.9	1000 @ 1 A cm ⁻²	22
20	H _{3.8} Ir _{1-x} Ru _x O ₄	255	56.5	/	0.75 Ir	2.11 @ 2 A cm ⁻²	1100 @ 1 A cm ⁻²	23
21	Sr-IrO _x	240	48	N115 60°C	1.0 Ir	2.0	520 @ 1 A cm ⁻²	24
22	Mn _{0.2} RuO ₂	188	57	N115	/	2.0	180 @ 1 A cm ⁻²	25
23	RuTiO _x	198	63	/	1 cat.	1.54 @ 1 A cm ⁻²	100 @ 0.5 A cm ⁻²	26
24	Ta _{0.1} Ru _{0.9} O _{2-x}	226	47.1	/	0.8 cat.	2 @ 2 A cm ⁻²	2800 @ 1 A cm ⁻²	27
25	IrO ₂ /TiO ₂ -1	247	56.6	N115 60°C	0.3 Ir	1.787 @ 2 A cm ⁻²	350 @ 1 A cm ⁻²	28
26	MD-RuO ₂ -BN	196	52.3	N115 80°C	2 cat.	1.8 @ 2 A cm ⁻²	50 @ 1 A cm ⁻²	29
27	Er-RuO ₂	200	45	N117 80°C	3 cat.	1.837	100 @ 1 A cm ⁻²	30
28	Ir-Mn-Ov	166	38	/	0.1 Ir	1.60 @ 1 A cm ⁻²	1000 @ 0.2 A cm ⁻²	31
29	Ir-RuO ₂	167	48.2	N115 80°C	3 cat.	1.60 @ 1 A cm ⁻²	300 @ 1 A cm ⁻²	32
30	Ir/MnO _x	238	42.5	N117 80°C	0.2 Ir	1.8 @ 2 A cm ⁻²	300 @ 1 A cm ⁻²	33
31	Li-IrO _x	314	50.0	N212 80°C	0.4 Ir	1.74	100 @ 2 A cm ⁻²	34
32	Ir/IrO _x ~SO ₃ H	233	45.1	N212 80°C	1.0 Ir	1.75	1100 @ 1 A cm ⁻²	35
33	CoOOH	/	/	N212 80°C	2.0 cat.	2.36 @ 2 A cm ⁻²	400 @ 0.1 A cm ⁻²	36
34	LRCO	141	88.0	/	1.8 cat.	1.75 @ 1 A cm ⁻²	720 @ 1 A cm ⁻²	37
35	IrO ₂ (101) monolayer	230	44.73	N115 80°C	1.5 Ir	1.70 @ 2 A cm ⁻²	10000 @ 1.5 A cm ⁻²	38
36	Co _{0.3} Ru _{0.7} O ₂ -TiO ₂	153	40.17	/	2.0 cat.	1.83 @ 2 A cm ⁻²	1060 @ 0.5 A cm ⁻²	39
37	W-NiCo ₂ O ₄	289	93.8	/	/	1.78 @ 1 A cm ⁻²	280 @ 1 A cm ⁻²	40
38	4f-Nd-RuO ₂	214	62.0	N115 60°C 0.1 M HClO ₄	2.0 cat	1.83 @ 0.1 A cm ⁻²	200 @ 0.1 A cm ⁻²	41
39	Sb-RuO ₂	220	55.5	N115 80°C	3.0 cat	1.74 @ 2 A cm ⁻²	300 @ 0.1 A cm ⁻²	42

40	RuO ₂ /LiCoO ₂	150	51.97	/	4.0 _{cat}	1.68 @ 1 A cm ⁻²	2000 @ 1 A cm ⁻²	43
41	LD-B/RuO ₂	175	49.9	/	2.0 _{cat}	1.63 @ 1 A cm ⁻²	300 @ 0.25 A cm ⁻²	44
42	Ru _{0.9} Ir _{0.1} O _x	/	48	/	2.0 _{cat}	1.74	500 @ 1 A cm ⁻²	45
43	Cr _{0.1} Sn _{0.1} Ru _{0.8} O ₂	178	47.3	80°C	/	1.77	1000 @ 0.5 A cm ⁻²	46
44	Co-Ru@RuO ₂	203	37.9	N115 60/80°C	0.5 _{cat}	1.58 @ 1 A cm ⁻²	200 @ 0.5 A cm ⁻²	47
45	3MS-IrO ₂	/	46	N115 80°C	2.0 _{cat}	1.58 @ 1 A cm ⁻²	2700 @ 5 A cm ⁻²	48

Stability marked with an asterisk (*) usually indicates the duration until stability degradation, while unmarked values refer to the operational or testing duration. References lacking voltage data at 3 A cm⁻² are marked accordingly. Mark (PGM) denotes platinum-group-metal loading, while (cat.) refers to the total solid mass of the catalyst.

Supplementary Table 2. DFT-derived charge parameters of the samples.

	Ru-Bader	O $2p$ (eV)	Ru $3d$ (eV)	e_g/t_{2g}
Rutile-RuO ₂	1.599	-4.50	-0.60	1.969
Y _{0.1} Ir _{0.2} Ru _{0.7} O _x	1.578	-4.19	-0.57	1.786
Ir _{0.2} Ru _{0.8} O _x	1.583	-4.32	-0.51	1.924

Supplementary Table 3. Ru K-edge EXAFS fitting results of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$.

	Shell	N^a	R (Å)	σ^2 (Å)	E^0 (eV)	R factor
Ru Foil	Ru-Ru	12*	2.675	0.00542	-0.033	0.0094
	Ru-O	6*	1.973	0.00588		
Rutile-RuO ₂	Ru-Ru ₁	2*	3.187	0.00762	-3.816	0.0144
	Ru-Ru ₂	8*	3.541			
$\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$	Ru-O	5.7	2.039	0.01938	-6.274	0.0190
	Ru-Ru ₁	1.8	3.078	0.00653		
	Ru-O	4.4	1.969	0.00507		
$\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$	Ru-Ru ₁	1.3	3.186	0.00618	-1.895	0.0142
	Ru-Ru ₂	9.0	3.534			

Supplementary Table 4. The average Ru-O bond lengths at several different positions after model relaxation (unit: Å)

	Ru-O short	Ru-O medium	Ru-O long
RuO ₂ Model	/	1.978	/
RuIrO _x Model	1.946	1.986	/
YRuIrO _x Model	1.937	1.970, 1.991	2.028

Supplementary Table 5. Ir L_{III} -edge EXAFS fitting results of $Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$.

	Shell	N^a	R (Å)	σ^2 (Å)	E^0 (eV)	R factor
Ir Foil	Ir-Ir	12*	2.71255	0.00647	7.996	0.0087
Rutile- IrO_2	Ir-O	6*	1.98200	0.00763	10.347	0.0181
$Y_{0.1}Ir_{0.2}Ru_{0.7}O_x$	Ir-O	5.04	2.05716	0.00923	9.523	0.0115
$Ir_{0.2}Ru_{0.8}O_x$	Ir-O	5.27	1.99527	0.01144	9.309	0.0103

Supplementary Table 6. The ICP-MS results of metal leaching content from the water source during the stability testing of $\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$ in PEMWE (units: ppb).

Sampling Time (h)	Y	Ru	Ir
12	0.035	3.250	2.250
24	0.000	10.300	0.019
36	0.000	9.820	0.000
48	0.000	8.000	0.000
100	0.000	0.116	0.044
500	0.000	0.042	0.063
1000	0.000	0.036	0.058

Supplementary Table 7. Benchmarking S-numbers of representative OER catalysts.

	S-number _{Ru}	S-number _{Ir}	S-number _{PGM}
Y _{0.1} Ir _{0.2} Ru _{0.7} O _x , 24h	1.06×10 ⁷	1.14×10 ⁸	9.70×10 ⁶
Y _{0.1} Ir _{0.2} Ru _{0.7} O _x , 1000h	1.56×10 ⁸	4.54×10 ⁹	1.52×10 ⁸
Crystal IrO ₂ ⁴⁹		10 ⁶ ~10 ⁷	
Ru-RuO ₂ -Sn ⁵⁰	6.7×10 ⁶		
IrO ₂ (101) monolayer ³⁸		4.48×10 ⁶	
IrRuO _x /MnO _x ⁵¹	3.82×10 ³	5.98×10 ⁴	3.55×10 ³

The S-number was calculated as the number of evolved oxygen molecules divided by the number of dissolved site atoms (Ru/Ir)⁴⁹. The amount of evolved oxygen was determined as:

$$n_{\text{O}_2} = \frac{\text{Faradaic efficiency} \times n_{\text{e}^-}}{4}$$

where the Faradaic efficiency was assumed to be 100%. The numbers of dissolved Ru and Ir atoms were obtained by integrating the atom dissolution rate–time curves constructed from the ICP-MS results.

Supplementary Table 8. ICP-MS results from diluted MEA. (unit: ppb)

Elements	1st sample	2nd sample	3rd sample	Average
Y	7.575	7.528	6.678	7.260
Ir	48.313	50.118	49.389	49.273
Ru	236.029	244.964	243.968	241.654

Supplementary Table 9. The ratio of the MS signal integral $^{18}\text{O}^{18}\text{O}/^{16}\text{O}^{18}\text{O}$ in the samples in H_2^{18}O .

Segments	$\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$	$\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$
1	5.800	10.400
2	5.710	10.200
3	5.770	10.300
4	5.980	10.400
5	6.210	10.500
6	6.480	10.700

Supplementary Table 10. The ratio of the MS signal integral $^{16}\text{O}^{16}\text{O}/^{16}\text{O}^{18}\text{O}$ in the samples in H_2^{16}O .

Segments	$\text{Y}_{0.1}\text{Ir}_{0.2}\text{Ru}_{0.7}\text{O}_x$	$\text{Ir}_{0.2}\text{Ru}_{0.8}\text{O}_x$
1	1.420	29.100
2	1.700	30.500
3	1.980	31.800
4	2.260	35.100
5	2.550	40.500
6	2.900	47.400

References

1. Liu, K. *et al.* Puffing ultrathin oxides with nonlayered structures. *Sci. Adv.* **8**, eabn2030 (2022).
2. Over, H. Surface chemistry of ruthenium dioxide in heterogeneous catalysis and electrocatalysis: from fundamental to applied research. *Chem. Rev.* **112**, 3356–3426 (2012).
3. McCrory, C. C. L. *et al.* Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *J. Am. Chem. Soc.* **137**, 4347–4357 (2015).
4. Ferner, K. J. & Litster, S. Composite anode for PEM water electrolyzers: lowering iridium loadings and reducing material costs with a conductive additive. *ACS Appl. Energy Mater.* **7**, 8124–8135 (2024).
5. Qian, F. *et al.* High-entropy RuO₂ catalyst with dual-site oxide path for durable acidic oxygen evolution reaction. *Nat. Commun.* **16**, 6894 (2025).
6. Kuznetsova, E. *et al.* Identification of the byproducts of the oxygen evolution reaction on Rutile-type oxides under dynamic conditions. *J. Electroanal. Chem.* **728**, 102–111 (2014).
7. Xu, J. *et al.* IrO_x·nH₂O with lattice water-assisted oxygen exchange for high-performance proton exchange membrane water electrolyzers. *Sci. Adv.* **9**, eadh1718 (2023).
8. Liu, H. *et al.* Eliminating over-oxidation of ruthenium oxides by niobium for highly stable electrocatalytic oxygen evolution in acidic media. *Joule* **7**, 558–573 (2023).
9. Sun, P. *et al.* Designing 3d transition metal cation-doped MRuO_x as durable acidic oxygen evolution electrocatalysts for PEM water electrolyzers. *J. Am. Chem. Soc.* **146**, 15515–15524 (2024).
10. Tao, L. *et al.* Mass-efficient catalyst layer of hierarchical sub-nanosheets on nanowire for practical proton exchange membrane electrolyzer. *Joule* **8**, 450–460 (2024).
11. Hu, C. *et al.* Misoriented high-entropy iridium ruthenium oxide for acidic water splitting. *Sci. Adv.* **9**, eadf9144 (2023).
12. Wen, Y. *et al.* Stabilizing highly active Ru sites by suppressing lattice oxygen participation in acidic water oxidation. *J. Am. Chem. Soc.* **143**, 6482–6490 (2021).
13. Su, H. *et al.* Tensile straining of iridium sites in manganese oxides for proton-exchange membrane water electrolyzers. *Nat. Commun.* **15**, 95 (2024).
14. Zhao, S. *et al.* Constructing regulable supports via non-stoichiometric engineering to stabilize ruthenium nanoparticles for enhanced pH-universal water splitting. *Nat. Commun.* **15**, 2728 (2024).

15. Xue, Y. *et al.* Stabilizing ruthenium dioxide with cation-anchored sulfate for durable oxygen evolution in proton-exchange membrane water electrolyzers. *Nat. Commun.* **14**, 8093 (2023).
16. Zhu, W. *et al.* Stable and oxidative charged Ru enhance the acidic oxygen evolution reaction activity in two-dimensional Ruthenium-Iridium oxide. *Nat. Commun.* **14**, 5365 (2023).
17. Han, X. *et al.* Theoretical prediction and experimental verification of IrO_x supported on titanium nitride for acidic oxygen evolution reaction. *J. Am. Chem. Soc.* **146**, 16499–16510 (2024).
18. Shi, Z. *et al.* Enhanced acidic water oxidation by dynamic migration of oxygen species at the Ir/Nb₂O_{5-x} catalyst/support interfaces. *Angew. Chem. Int. Ed.* **61**, e202212341 (2022).
19. Chang, J. *et al.* Oxygen radical coupling on short-range ordered Ru atom arrays enables exceptional activity and stability for acidic water oxidation. *J. Am. Chem. Soc.* **146**, 12958–12968 (2024).
20. Chen, D. *et al.* Boron-induced interstitial effects drive water oxidation on ordered Ir-B compounds. *Angew. Chem. Int. Ed.* **63**, e202407577 (2024).
21. Hao, S. *et al.* Torsion strained iridium oxide for efficient acidic water oxidation in proton exchange membrane electrolyzers. *Nat. Nanotechnol.* **16**, 1371–1377 (2021).
22. Wang, Y. *et al.* Supported IrO₂ nanocatalyst with multilayered structure for proton exchange membrane water electrolysis. *Adv. Mater.* **36**, 2407717 (2024).
23. Tang, J. *et al.* Ruthenium single-atom modulated protonated iridium oxide for acidic water oxidation in proton exchange membrane electrolyzers. *Adv. Mater.* **36**, 2407394 (2024).
24. Zhang, W. *et al.* Strontium doped IrO_x triggers direct O-O coupling to boost acid water oxidation electrocatalysis. *Angew. Chem. Int. Ed.* **64**, e202418456 (2025).
25. Ji, Q. *et al.* Operando identification of the oxide path mechanism with different dual-active sites for acidic water oxidation. *Nat. Commun.* **15**, 8089 (2024).
26. Hu, W. *et al.* Doping Ti into RuO₂ to accelerate bridged-oxygen-assisted deprotonation for acidic oxygen evolution reaction. *Adv. Mater.* **37**, 2411709 (2025).
27. Zhang, J. *et al.* Tantalum-stabilized ruthenium oxide electrocatalysts for industrial water electrolysis. *Science* **387**, 48–55 (2025).
28. Yang, C. *et al.* Surface hydroxylation engineering to boost oxygen evolution reaction on IrO₂/TiO₂ for PEM water electrolyzer. *Appl. Catal. B Environ. Energy* **358**, 124462 (2024).

29. Chen, D. *et al.* Bicontinuous RuO₂ nanoreactors for acidic water oxidation. *Nat. Commun.* **15**, 3928 (2024).
30. Li, L. *et al.* Lanthanide-regulating Ru-O covalency optimizes acidic oxygen evolution electrocatalysis. *Nat. Commun.* **15**, 4974 (2024).
31. Lin, H. Y. *et al.* Enriched oxygen coverage localized within Ir atomic grids for enhanced oxygen evolution electrocatalysis. *Adv. Mater.* **36**, 2408045 (2024).
32. Wu, H. *et al.* Atomically engineered interfaces inducing bridging oxygen-mediated deprotonation for enhanced oxygen evolution in acidic conditions. *Nat. Commun.* **15**, 10315 (2024).
33. Wang, D. *et al.* Ir-O-Mn embedded in porous nanosheets enhances charge transfer in low-iridium PEM electrolyzers. *Nat. Commun.* **16**, 181 (2025).
34. Kang, J. *et al.* Active and stable layered alkali iridates efficiently catalyze oxygen electroevolution in low-Ir proton-exchange membrane (PEM) water electrolyzers. *J. Am. Chem. Soc.* **147**, 45230–45239 (2025).
35. Li, J. *et al.* Surface sulfonic-group bonded oxygen evolution catalyst for proton exchange membrane water electrolysis. *Nat. Commun.* **16**, 9910 (2025).
36. Huang, J. *et al.* Directly synthesized cobalt oxyhydroxide as an oxygen evolution catalyst in proton exchange membrane water electrolyzers. *Nat. Commun.* **16**, 7518 (2025).
37. Zhu, S. *et al.* Mixed ionic–covalent bonds achieve durable acidic water oxidation. *J. Am. Chem. Soc.* **147**, 39494–39504 (2025).
38. Yang, D. *et al.* Single-faceted IrO₂ monolayer enabling high-performing proton exchange membrane water electrolysis beyond 10,000 h stability at 1.5 A cm⁻². *Nat. Commun.* **16**, 7236 (2025).
39. Liang, J. *et al.* Dual-Site cobalt-doped RuO₂/TiO₂ electrocatalyst enables stable and cost-efficient acidic oxygen evolution for PEM water electrolysis. *J. Am. Chem. Soc.* **147**, 39781–39795 (2025).
40. Li, S. *et al.* Oxophilic sites mediated dynamic oxygen replenishment to stabilize lattice oxygen catalysis in acidic water oxidation. *J. Am. Chem. Soc.* **147**, 33770–33779 (2025).
41. Zhang, X. *et al.* 4f-modified Ru-O polarity as a descriptor for efficient electrocatalytic acidic oxygen evolution. *Nat. Commun.* **16**, 6921 (2025).
42. Lin, X. *et al.* Electronic tuning of RuO₂ polarizes metal–oxygen redox for proton exchange membrane water electrolysis. *Nat. Commun.* **16**, 8709 (2025).

43. Wang, L. *et al.* Modulating the covalency of Ru-O bonds by dynamic reconstruction for efficient acidic oxygen evolution. *Nat. Commun.* **16**, 3502 (2025).
44. Chen, G. *et al.* A Long-range disordered RuO₂ catalyst for highly efficient acidic oxygen evolution electrocatalysis. *Angew. Chem. Int. Ed.* **63**, e202411603 (2024).
45. Xu, J. *et al.* *Operando* Insights into Bridging Oxygen-Driven RuO_x Lattice Collapse and its Mitigation Strategy for Durable Industrial PEMWE. *Angew. Chem. Int. Ed.* **65**, e20766 (2026).
46. Bao, J. *et al.* Electronic structure-engineered proton depletion interfaces on ternary RuO₂ for ultra-stable kilowatt electrocatalysis. *Angew. Chem. Int. Ed.* **64**, e202515362 (2025).
47. Chen, J. *et al.* Cobalt-doped Ru@RuO₂ core-shell heterostructure for efficient acidic water oxidation in low-Ru-loading proton exchange membrane water electrolyzers. *J. Am. Chem. Soc.* **147**, 8720–8731 (2025).
48. Wei, C. *et al.* Dynamic template reconstruction induced mesoporous iridium catalysts for high-current-density PEMWE. *Joule* **9**, 102058 (2025).
49. Geiger, S. *et al.* The stability number as a metric for electrocatalyst stability benchmarking. *Nat. Catal.* **1**, 508–515 (2018).
50. Song, Y. *et al.* Sub-4 nm Ru-RuO₂ schottky nanojunction as a catalyst for durable acidic water oxidation. *J. Am. Chem. Soc.* **147**, 13775–13783 (2025).
51. Kang, J. *et al.* Highly active IrRuO_x/MnO_x electrocatalysts with ultralow anode PGM demand in proton exchange membrane electrolyzers. *Adv. Energy Mater.* **16**, 2405758 (2026).