Supplementary Note 6
(Details of Domain Adaptation-Assisted DFT Theoretical Simulation)
for

Leveraging Data Mining, Active Learning, and Domain Adaptation in a Multi-Stage, Machine Learning-Driven Approach for the Efficient Discovery of Advanced Acidic Oxygen Evolution Electrocatalysts

Rui Ding *et al.*

*Corresponding author. Email: junhongchen@uchicago.edu, chenyuxin@uchicago.edu

Supplementary Note Discussion SND 6-1
Generation of DFT-Calculated Dataset
Readers could check the corresponding scripts in the online repository's directory "DFT Structures Generate".
Doping Structure Generation
In our study, we employed a Python-based computational approach to generate the random doping of RuO_2 (110) slabs with two distinct elements. The process begins with the selection of a RuO_2 structure from the Materials Project dataset, using its material ID ("mp-825"). This structure is then standardized and reoriented to ensure the correct orientation of the (110) surface. Subsequently, we generate slabs with a minimum thickness of 12 Å and a vacuum padding of 15 Å, focusing on the (1,1,0) Miller index surface. To accommodate larger surface areas and enable diverse doping configurations, these slabs are expanded into a supercell format, scaling by a factor of 2 along the x and y axes. The final crystal has 96 atoms, 64 O atoms and 32 Ru atoms with part of the Ru atoms replaced randomly.

The core of our doping algorithm involves the random substitution of Ru atoms in the RuO_2 (110) slab. For each simulation run, two elements are randomly chosen from a predefined list of 23 potential dopants, including transition metals like K, Ca, and Fe, among others. We would name them "Element Set S", representing the commonly studied doping elements by previous domain experts:

Element Set S:

K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Rb, Sr, Y, Zr, Nb, Mo, Tc, Rh, Cs, Ba, Os, Re, Ir

The substitution process adheres to a controlled randomness, governed by a seed value for reproducibility. Each Ru atom in the slab is potentially replaced by one of the selected dopants, with the substitution ratios varying randomly between 5% and 35% for each element. This ratio is determined by a uniform random distribution, ensuring a diverse range of doping configurations across different simulation runs.

The reason we chose to generate random structures with only two dopant elements is based on experimental observations that additional elements such as Nd and Pr are present in trace amounts, significantly less than 1/96 in our system. Furthermore, introducing a third dopant would considerably expand the sampling space and, consequently, the cost of dataset preparation. Hence, we decided to proceed under the assumption that the presence of a third element would not lead to significant variations in energy or errors. Nevertheless, the success of the domain adaptation process later confirmed that the ML committee we trained, especially committee S-T, possesses strong generalization abilities. The ultra-high R^2 values of the corresponding member models indicate their accuracy in capturing the overall trends and relative changes within the data. This level of reliability is crucial for predicting both the direction and relative magnitude of changes in crystal structures, given the vast array of potential doping elements and ratios. Therefore, we used committee S-T directly to search for stable doping configurations in previously experimentally screened samples. Ultimately, the high consistency between the DFT results and experimental evaluations supports the reliability of our approach, particularly demonstrating the origins of sample C's superior activity and stability. This post hoc validation reinforces the validity of our methodology.

After the substitution, the modified slab structures are saved in the VASP POSCAR format for further lattice relaxation, and we would name the corresponding OER intermediate adsorption energies in a typical well-known previously reported paradigm by Norskov et al. in 2011(*1*). Adsorbate evolution mechanism (AEM) is considered here for computing the adsorption energy

of OER process via intermediates: O, OH, and OOH. We would name this part of dataset with a larger number (3,973 structures) but less choices of doping elements (Element Set S) "Dataset S".

To explore more possibilities as we have stated in the main text, we also generated doping structures for another set that has included rare-earth elements, as we name them "Element Set T":

Element Set T:

Ga, In, Sn, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Hg, Tl, Pb, Bi, Li, Al

And we applied a dual-selection mechanism for element set T, which is governed by a probabilistic model where there's a 50% chance of choosing one element from each element set (S and T) or only selecting both elements from Set T. By this method, we can obtain another dataset "Dataset T" which has a smaller number (963 structures) of samples, but its describing domain has included element set T.

Intermediate Adsorption Structures

As for the next step, generation of the three different oxygen intermediates: O, OH, and OOH, we have also designed an automatic python script based on a simple hypothesis to generate their initial adsorption structures on the as-optimized (by DFT calculation software Vienna Ab-initio Simulation Package, VASP) doped RuO_2 structures. In our computational approach, we addressed the challenge of identifying optimal adsorption sites on doped RuO_2 surfaces, which possess multiple inequivalent sites due to doping. To systematically determine the most favorable adsorption sites, we utilized the AdsorbateSiteFinder functionality from the pymatgen library by Materials Project, a tool commonly used for identifying potential adsorption sites on crystal surfaces. Our strategy involved generating a series of possible adsorption structures for different adsorbates (O, OH, and OOH molecules) on the doped RuO_2 slabs. Given the complexity of the surface due to various dopants, we focused on finding the nearest adsorption site to the original Ru atoms in the RuO_2 lattice. This was achieved by calculating the distances from the adsorbed oxygen atom of the adsorbate to all surface atoms, excluding certain elements like O, F, I, and Br, to avoid unrealistic adsorption scenarios. The site closest to the adsorbed oxygen atom was then selected as the preferred adsorption site. This method allowed us to identify adsorption sites systematically and consistently across different doped structures, ensuring a focused and comparative analysis of adsorption characteristics on these complex surfaces.

By the above method, we acknowledge that our approach of considering only one adsorption site per structure may not encompass all possible adsorption scenarios, potentially overlooking some more favorable sites. However, this methodology was adopted due to practical constraints and is justified by several key considerations. Firstly, the computational cost associated with exploring all possible adsorption sites on large supercells, containing up to 96 atoms, is prohibitively high. Such exhaustive calculations would require significant computational resources and time, which may not be feasible for a study of this scale. Secondly, the complexity of the doped RuO_2 supercells adds another layer of challenge. The presence of various dopants introduces a multitude of inequivalent sites, making a comprehensive search for the optimal adsorption site increasingly complex. By focusing on the nearest site to the original Ru atoms, we implement a consistent and systematic approach that allows for a comparative analysis across different doped structures. Furthermore, our chosen method aligns with the primary objective of our study, which is to understand the relative effects of doping on adsorption characteristics rather than

determining the absolute best adsorption site for each structure. This approach provides valuable insights into how doping influences adsorption behavior, which is central to our research goals. Lastly, this strategy also allows for a more streamlined and efficient workflow, enabling the analysis of a larger number of structures within a reasonable timeframe. While this method may not capture the full complexity of the system, it strikes a balance between computational feasibility and the need to generate meaningful, comparative data on the impact of doping in RuO_2.

In conclusion, our focus on proximity to Ru atoms and leveraging the capabilities of pymatgen provide a robust and efficient way to explore adsorption phenomena on doped RuO_2 surfaces, accommodating the diversity and complexity introduced by various dopants.

High Throughput DFT Calculation

In our computational DFT study, the relaxation of the previously mentioned randomly doped RuO_2 (110) slabs as well as the adsorption structure of oxygen-containing intermediates were generated by python script leveraging different libraries but were all further calculated for structure optimization using the VASP package. The relaxation process aims to optimize the crystal structure by minimizing the forces and stress on the atoms. The key parameters for our simulations were meticulously chosen to ensure accuracy and efficiency. First, KPOINTS are set to gamma point 1*1*1. The plane wave basis set was defined with a cut-off energy of 500 eV (ENCUT), ensuring sufficient accuracy for our system. The precision of the calculations was set to "Accurate" (PREC). The electronic relaxation algorithm was set to "Veryfast" (ALGO), suitable for quick convergence in large systems. Gaussian smearing (ISMEAR = 0) with a smearing value of 0.05 eV (SIGMA) was used to aid in the electronic convergence, particularly important for systems with a metallic character. The self-consistent field (SCF) iterations were controlled with a maximum of 300 steps (NELM) and a minimum of 5 steps (NELMIN), with an energy convergence criterion set to 1E-04 eV (EDIFF). For the ionic relaxation, we used the conjugate gradient algorithm (IBRION = 2) with a maximum of 300 ionic steps (NSW) and allowed for the relaxation of the cell shape and volume in addition to the ion positions (ISIF = 3). The ionic convergence criterion was set to -0.05 eV/Å (EDIFFG), ensuring that the forces on the ions were sufficiently minimized. The symmetry was not imposed during the relaxation (ISYM = 0) to allow for the full exploration of the potential energy surface. These settings were carefully chosen to balance computational efficiency with the accuracy required for investigating the structural and electronic properties of the doped RuO_2 (110) slabs.

In the calculations of adsorbed intermediates such as O, OH, and OOH on the as-optimized doped RuO_2 (110) slabs by the previous step, we implemented a more stringent convergence criterion to ensure a higher accuracy in capturing the subtle interactions between the adsorbate and the surface. Specifically, the energy convergence criterion for the electronic SCF iterations was set to a tighter value of 1E-05 eV, compared to 1E-04 eV used for the slab relaxation. This adjustment provides a more precise description of the electronic structure in the presence of adsorbates. Additionally, the ionic relaxation convergence criterion was set to -0.01 eV/Å , a more stringent threshold than the -0.05 eV/Å used for the bare slabs, ensuring a more accurate optimization of the adsorbate-substrate system. The ISIF parameter was set to 2, focusing on the relaxation of ion positions while keeping the cell shape and volume fixed, which is appropriate for adsorption studies where the primary interest is in the interaction of adsorbates with the surface atoms.

In addressing the concerns regarding the absence of DFT+U corrections in our computational study, it is important to emphasize the focus on relative comparisons rather than absolute quantum chemical properties. Our primary objective is to elucidate the effects of doping on RuO_2, where the consistency in computational methodology across the entire dataset, especially when compared to undoped RuO_2, is crucial. The standard DFT approach, without the addition of U corrections, provides sufficient accuracy for this comparative analysis. Moreover, the diversity and complexity of elements involved in the dataset make the application of DFT+U less straightforward, as it would require a meticulous, element-specific calibration of U parameters. By maintaining a uniform computational strategy, we ensure that the comparative insights drawn are both reliable and scientifically valid, focusing on the relative impact of doping rather than the absolute accuracy of electronic correlations.

Supplementary Note Discussion SND 6-2

Reproducibility Details of DFT Surrogate ML Committee Training and Domain Adaptation

The script of this part is stored at directory "Machine Learning Databases and Script/DFT Domain Adaptation" in the GitHub repository.

Descriptor Conversion

In the research presented, we developed a novel approach for transforming crystal structures into matrices suitable for training of the ML committee members as input. This transformation was achieved through the application of several chemical descriptors, notably the Smooth Overlap of Atomic Positions (SOAP), Sine Matrix, and other descriptors like Ewald Sum Matrix and Atom-Centered Symmetry Functions (ACSF)(*2*).

The primary focus was on the generation of a comprehensive descriptor matrix that encapsulates the intricate details of crystal structures. To this end, we utilized the Sine Matrix and Ewald Sum Matrix, both of which are known for their ability to effectively describe periodic systems. The Sine Matrix was configured with parameters such as a maximum of 96 atoms, sorted L2 permutation, and non-sparse, non-flattened output. Similarly, the Ewald Sum Matrix was set up with a non-flattened, non-sparse output and no permutation, catering to a maximum of 96 atoms. Further enhancing the descriptor matrix, we incorporated the ACSF, which was parameterized to include a range of species and configured with a cutoff radius (r_{cut}), periodicity, and specific G2 and G4 parameters. This inclusion of ACSF allowed for a more nuanced representation of the atomic environment, capturing essential chemical and physical properties.

The resultant descriptor matrix, with dimensions 768*969, represents a comprehensive and detailed encapsulation of the crystal structures. This matrix serves as the input for subsequent machine learning models, facilitating the accurate prediction of properties like adsorption energies and catalytic activities. The approach demonstrates a significant advancement in the field of materials science, offering a robust method for converting complex crystal structures into a format amenable to advanced machine learning techniques.

Committee S and T Training

After preparation and construction of the dataset, we would use dataset S to train committee S, the same for dataset T and committee T. Similar to what we have employed in the previous DASH loop, we choose to use different models to train on the same dataset to obtain a robust ML committee. The ML committee for the DFT part includes following algorithms and deep learning structures:

(#1) Bidirectional LSTM: This model consists of a bidirectional Long Short-Term Memory (LSTM) layer with 100 units, followed by a dense output layer.

(#2) Simple RNN: It features two layers of Simple Recurrent Neural Networks (RNN) with 100 units each, and a dense output layer.

(#3) GRU: This model employs two Gated Recurrent Unit (GRU) layers with 100 units each, followed by a dense output layer.

(#4) Simple One-Layer CNN: A single-layer Convolutional Neural Network (CNN) with 32 filters, followed by max pooling, flattening, and two dense layers.

(#5) Multilayer CNN: A deeper CNN with three convolutional layers (64, 32, and 16 filters), each followed by max pooling, then flattening, and two dense layers.

(#6) CNN-LSTM: Combines CNN and LSTM, starting with two convolutional layers and max pooling, followed by flattening, a repeat vector, an LSTM layer, and two time-distributed dense layers.

(#7) Single-Layer TCN: A Temporal Convolutional Network (TCN) with 64 filters, various dilation rates, and causal padding, followed by a dense output layer.
(#8) Multilayer TCN: Similar to the single-layer TCN but with an additional TCN layer before the dense output layer.
(#9) Advanced CNN: A CNN with three convolutional layers (128, 64, and 32 filters), each followed by max pooling, then flattening, and two dense layers.
(#10) Conv2D CNN: A 2D CNN with two convolutional layers (32 and 16 filters), each followed by max pooling, flattening, and two dense layers.
In our data preprocessing stage for the deep learning model, we employed various scaling techniques to normalize the input and output data. Specifically, we used MinMaxScaler to scale the input data (X) and RobustScaler for the output data (y), ensuring that they are appropriately scaled for neural network training. The MinMaxScaler was configured to transform the data within the range of 0 to 1, while the RobustScaler was used to scale the output data, making it more robust to outliers.
We explored different combinations of input and output scalers, including MinMaxScaler, StandardScaler, MaxAbsScaler, and RobustScaler, to determine the best normalization method for each prediction target (SLAB, O, OH, OOH) in our dataset S. This comprehensive approach involved training **(#10)** model with each scaler combination and comparing their performance based on R^2 scores. The objective was to identify the most effective normalization technique for each target, ensuring optimal model performance and accurate predictions.
In this section, the training process was rigorously structured. We applied overall 10-fold CV(*3*) to ensure the robustness and generalizability of the models. This approach also facilitated the identification of the best-performing model for each architecture. The models were evaluated based on several key metrics, including MSE, RMSE, MAE, and R^2. And the bar plots like **Fig. 6B** represents the 10-fold average with error bar representing standard deviation of the 10-fold evaluation processes. Moreover, adhering to an optimistic evaluation method, we specifically retained the model from the fold that demonstrated the highest R^2 value, employing this as our start point for subsequent domain adaptation processes. The adoption of an optimistic estimation strategy, where the best fold model is retained, serves to showcase the maximum potential of each model in ideal conditions. This approach is particularly crucial for demonstrating the effectiveness of new methods or architectures, as it provides insights into the upper limits of model performance. Furthermore, by consistently applying this 'best fold' strategy across all models (Model S, Model T, and Model S-T), we establish a uniform benchmark for comparison. Although this might lead to an overestimation of each model's absolute performance, it ensures that the relative performance comparisons among the models remain valid and meaningful.

Domain Adaptation for Committee S-T
Domain adaptation, a form of transfer learning, is employed in machine learning to enhance the performance of a model on a new, but related, task by leveraging the knowledge gained while training on a different task. This technique is particularly advantageous in scenarios where a substantial dataset is available for one task (referred to as the source domain), but the dataset for the target task (the target domain) is limited.
Here, domain adaptation is implemented by adapting models initially trained on a source dataset (dataset S) to a new, related dataset (dataset T). The process encompasses several critical steps:

1.   **Model Selection**: Models previously trained on dataset S, namely committee S are chosen. These models have acquired specific features and patterns from dataset S, which are anticipated to be beneficial when applied to dataset T.
2.   **Fine-Tuning**: The chosen models undergo fine-tuning with dataset T. This step involves additional training where the models adjust their weights to better suit the new dataset. We have applied a random initial strategy namely use committee S's weight and bias in their network structures as the start point of training. Then the training epoch number is limited to finish the fine-tuning. To be noted, due to the fact that simple RNN and simple one-layer CNN shown inferior performances, they were deprecated and not included in committee S-T in the domain adaptation process because they lack of corresponding values to be existed.
3.   **Evaluation**: Post fine-tuning, the performance of the models on dataset T is evaluated using metrics as previously mentioned such as MSE, MAE, RMSE and R^2. These metrics provide insights into the accuracy and generalization capability of the models on the new dataset.
4.   **Iteration and Refinement**: The domain adaptation process is traversed through members in the ML committee of committee S, except for model #2 and #4. As we can see from the initial results from **Fig. 6B**, these two models have shown unstable and inferior performances that might not be worthy of fine-tuning to include in the committee S-T. Hence, they are not needed in our domain adaptation processes in committee S-T. We vividly represented this idea using two trash bin icons.

Domain adaptation is a strategic approach in fields like materials science, where acquiring extensive datasets can be resource intensive. By applying knowledge from a well-developed source domain, the development time and resources required for modeling in the target domain can be significantly reduced, thus enhancing the efficiency of the research process. And in our work, by our results presented in **Fig. 6B** and **Figs. S32-S35**, such success is proven to be effective and robust. To be noted, although in **Figs. S32**-**S35** we still use "Committee S", "Committee S", "Committee S-T" for situations with adsorbates on the slab, in the main text, Committee S-T in the context still refer to that we presented in **Fig. 6B**, namely the models are trained to predict the slab energy. That is because Committee S-T's main purpose is to help us quickly find the proper stable doping configuration once the dopant amount are given like experimentally synthesized samples A~D.

Supplementary Note Discussion SND 6-3
Surface OER Catalysis Simulation
As delineated in the main text, the same strategy of how to use a ML model committee to search for optimal solution is adopted here. Namely, like the last step in DASH was utilize, we would use the weighted average of the predictions from each member from the committee S-T to determine the expected value of a certain doping configuration. And the uncertainty is also defined by the variance generated in the predictions among the committee members. Committee S-T's output is the slab energy after relaxation, and its input is the doping configuration in the slabs, like in **Fig. 6C** we have illustrated. Therefore, GA was employed to identify the potentially lowest energy configurations for samples A ~D

After we have obtained the doping configurations of samples by utilizing committee S-T, the next step is to calculate the energies of the corresponding slabs. We have considered different scenarios: clean slab with no coverage species, and that with O and OH already adsorbed around the catalytic site. This type of surface coverage exploration is based on the well-recognized previous reports by Ulissi and Norkov(*4, 5*). Then, the slab energy with O, OH, OOH intermediate species adsorbed on the surface after relaxation were calculated, similar to that we have done in high throuput DFT calculation for preparing dataset S and dataset T. But a higher standard is adopted by the following changes: KPOINTS settings have been increased to 2*2*2 for better precision and for DOS calculation situation increased to 6*6*6. Besides, for both clean slab and that with adsorbates, the the ionic relaxation convergence criterion was set to -0.01 eV/Å and the energy convergence criterion for the electronic SCF iterations was set to a tighter value of 1E-05 eV.

Theoretical OER Overpotential Evaluation
As we have mentioned, we adopted commonly studied AEM mechanism for computing the OER theoretical overpotentials as previously reported by Norskov(*6*): * (Slab) +H_2O→*OH+H^++e^-; *OH→*O+H^++e^-; *O+H_2O→*OOH+H^++e^-; *OOH→*+O_2+ H^++e^-. Hence, the OER activity is strongly correlated with the Gibbs free energy change of adsorption. And the changes of Gibbs free energies of different reaction steps are computed using the common equation $\Delta G^* = \Delta E^* + \Delta E_{ZPE} - T\Delta S_H$. To be noted, ΔE_{ZPE} represents the zero-point energy difference between the adsorbed and gas phases. And ΔS_H stands for the entropy change at 1 atm while T stands for temperature (set as298.15 K). For simplicity, we use the reported values to conduct the corresponding thermodynamic correction item for the intermediates by constant values reported by Ulissi et al. for OER reactions(*5*).

Finally, the overpotentials of OER are computed in the typical previous reported way(*1*). The corresponding Gibbs free energy change descriptors of the intermediate states are $\triangle G_{OOH}^*$, $\triangle G_{OH}^*$, $\triangle G_O^*$, $\triangle G_1$, $\triangle G_2$, $\triangle G_3$, $\triangle G_4$.

Where $\triangle G_1$, $\triangle G_2$, $\triangle G_3$, $\triangle G_4$ represent the free energy difference of each step of OER AEM pathway from the first to the last:

$\triangle G_1 = \triangle G_{OH}^*$

$\triangle G_2 = \triangle G_O^* - \triangle G_{OH}^*$

$\triangle G_3 = \triangle G_{OOH}^* - \triangle G_O^*$

$\triangle G_4 = 4.92 \text{ eV} - \triangle G_{OOH}^*$

And the theoretical OER overpotential:

$\eta_{OER} = \max[\triangle G_1, \triangle G_2, \triangle G_3, \triangle G_4]/e - 1.23V$.

To be noted, our decision to choose AEM as the primary approach is based on the prevalent understanding that AEM is more dominant in RuO_2-based catalysts in acid, as evidenced by numerous experimental and theoretical studies([7-10]). Additionally, AEM provides a more straightforward framework for analyzing the Gibbs free energy changes associated with OER, making it a suitable choice for our initial investigations into these complex systems. And finally, due to our experimental results and calculation of the oxygen vacancy formation energy V_O, our samples are relatively stable against the lattice oxygen dissolution.

We also choose to investigate the LOM approach where the lattice oxygen vacancy would play an important role and has the potential to break the AEM theoretical limitation of 370 mV. Based on previous report([11]), the O vacancy (as we have calculated in **Fig. S41**, bridge vacancy) is serving as the adsorption site. And for the *OOH intermediate, two different configurations might be possible, on is *OOH still adsorbed on O vacancy site, one is that *OOH is break down into *O on the O vacancy site and *OH on the adjacent single metal site.

Theoretical Stability Evaluation

For evaluation of the stability of the samples, we have calculated three descriptors to comprehensively discussion this issue. First are the Gibbs free energy changes of water adsorption on the slab surfaces (clean surface). As we have shown in **Fig. S41**, we considered a 100% of water coverage based on the number of commonly studied unsaturated coordinated Ru sites. And calculated the free energy changes of water molecules adsorption behavior averaged to each molecule. Namely n equals to the number of water molecule (4 in our calculation since our initial slab is 2*2):

$$\triangle G_{H2O}{}^* = (G_{SLAB\ with\ adsorbed\ H2O} - (G_{SLAB} + n* G_{H2O}))/n$$

Based on previous studies of oxide surfaces([12-14]), it has been observed that surfaces exhibiting more favorable water molecule adsorption energies tend to exhibit higher surface stability. This stability is crucial as it directly influences the susceptibility of the surface to dissolution. The relationship between water adsorption energy and surface stability can be explained by the interaction forces between water molecules and the surface atoms. Stronger adsorption energy indicates more robust bonding interactions at the surface, which can effectively shield the surface from aggressive dissolution processes. Consequently, the ability of a surface to strongly adsorb water molecules is a key indicator of its stability and resistance to environmental degradation. And hence a negative $\triangle G_{H2O}{}^*$ would be indicating that the adsorption of water molecules on the surface is energetically favorable. This favorable adsorption energetically stabilizes the surface, making it less likely to dissolve in water. Essentially, the strong interaction between the water molecules and the surface creates a barrier that inhibits the breakdown and dissolution of the surface material into the aqueous environment. Thus, a more negative $\triangle G_{H2O}{}^*$ indicates that the surface is more stable and less prone to dissolution in water.

The second descriptor we adopted was the dissolution potential, U_{diss}. Reported by Norskov et al. as early as in 2007([15]) and recently utilized by the Kim group in studying OER/HER electrocatalysts([16, 17]) as an decisive descriptor to indicate the electrochemistry stability. It is calculated as the potential difference required to dissolve a metal atom from the catalyst into an aqueous solution under electrochemical conditions. U_{diss} is defined relative to the standard hydrogen electrode (SHE) and is expressed in volts. The calculation involves considering the standard dissolution potential of the bulk metal in an aqueous solution (pH = 0) and adjusting for the electron charge (e) and the number of electrons involved in the dissolution process (ne). Specifically, by the following equations:

$$U_{diss} = U_{diss(bulk\ metal)} - E_{stab}/ne\ (n=4)$$

E_{stab} is the the thermodynamic stability energy by considering the metal bulk cohesive energies. The E_{stab} is defined as the difference between the embedding energy E_{emb} and metal bulk cohesive energy E_{-coh}.

$E_{stab} = E_{emb} - E_{-coh}$

$E_{-coh} \equiv -E_{coh}$

$E_{emb} = E_{slab} - E_{slab\ with\ Ru\ vacancy} - E_{Ru}$

To be noted, E_{Ru} is the isolated Ru atom energy, and based on Norskov(*15*) and Kim et. al.'s reports(*16, 17*) as previously mentioned, the E_{-coh} and $U_{diss(bulk\ metal)}$ for pure Ru are 6.75 eV and 0.46 V respectively.

As for results, A U_{diss} value greater than 0 V relative to SHE indicates that the metal atoms are electrochemically stable, as they are strongly bound to the catalyst support, reducing the likelihood of metal dissolution under electrochemical reactions.

The third descriptor we utilized is the most used stability descriptor in OER electrocatalysts studies: the O vacancy formation energy(*3, 18-21*): $\triangle G_{VO}$ It is calculated by the following equation as its name suggests:

$\triangle G_{VO} = G_{slab} - 1/2 G_{O2} - G_{slab\ with\ O\ vacancy}$

It quantifies the thermodynamic feasibility of forming oxygen vacancies on the surface of catalyst materials, such as RuO_2-based systems. The energy required to create these vacancies directly impacts the material's structural integrity and its catalytic longevity under operating conditions. A lower $\triangle G_{VO}$ suggests that it is energetically easier to form vacancies, potentially leading to structural destabilization and decreased catalyst durability. Conversely, a higher $\triangle G_{VO}$ indicates that vacancy formation is less favorable, which corresponds to enhanced stability of the catalyst. Therefore, the oxygen vacancy formation energy is used as a primary indicator to assess the robustness of OER electrocatalysts, as it effectively predicts the material's resistance to degradation mechanisms such as over-oxidation and dissolution under harsh electrochemical environments. In our cases, we have also considered both scenarios for formation of O vacancies both in the plane or on the bridge sites. And by its definition, the one with lower $\triangle G_{VO}$ should be considered as the correct value.

Solvent Effect Simulation

All the default simulations are conducted in vacuum. For implicit solvent field, the solvation effects are accounted for by enabling the linearized Poisson–Boltzmann equation (LPBE) solver using. The dielectric constant of water (ε) is set to 78.4 (EB_K = 78.4), representing the relative permittivity of bulk water at room temperature. This approach effectively simulates the screening effects of the solvent without explicitly modeling water molecules, which significantly reduces computational cost. The implicit solvent model is particularly useful for studying electrochemical interfaces and catalytic reactions in aqueous environments, as it provides a reasonable approximation of the solvation energy and the associated stabilization of surface adsorbates.

To provide a more realistic representation of the OER process, we performed explicit solvent simulations. We further expanded the simulation slabs to a 2×2 supercell, resulting in 384 atoms (380 for LOM cases), and added a randomly generated water layer comprising 100 water molecules on the catalyst surface. To allow water molecules to relax and adopt physically meaningful positions and configurations, we conducted AIMD simulations under ambient temperature conditions (300 K) for 2 ps 1000 ionic steps for structural relaxation with time step of 2 fs, balancing computational efficiency and numerical stability; We also choose Langevin thermostat for temperature control without introducing unnecessary inertia into the system.

Following the AIMD relaxation, the configuration was fixed to represent a more realistic reaction surface for subsequent OER simulations. For these post-AIMD simulations, three active sites were randomly selected on the relaxed surface, to similarly conduct AEM and LOM pathways energy diagram analysis to obtain theoretical overpotential values under the effect of what we have crafted a more realistic water layer.

Supplementary Note Discussion SND 6-4
Calculation of OER Theoretical Overpotentials on other Possible Oxides
In this study, we first characterized that in our sample systems A~D, the predominant phase is RuO_2 doped with multiple metal element dopants, which is considered as the source of OER activity. This determination is based on the consensus in the field, supported by both DFT simulation calculations and experimental reports. However, as shown in **Fig. SN 5-23~Fig. SN 5-31** in **Supplementary Note 5**, there may still exist a small amount of oxide impurities that are not primarily RuO_2 in our system. To demonstrate that these impurities do not constitute the main source of OER activity, we can refer to the consensus obtained from authoritative studies in the field(*22-24*), whether based on theoretical calculations or experimental synthesis evaluations. Additionally, we conducted DFT theoretical simulations of the corresponding crystal facets shown in the XRD spectra, using the same DFT calculation configurations and creating slabs for these oxides following the same specifications. We then calculated the theoretical overpotentials under AEM and default vacuum condition with no surface coverage for these oxides without coverage, known to have the best OER activity as commonly discussed in the main text, as shown in **Table SN6-1** below. It can be observed that these oxides generally exhibit higher overpotentials compared to RuO_2, further proving that the multi-metal-doped RuO_2 discussed in the main text is indeed the source of activity.

Table SN 6-1 DFT-Calculated theoretical OER overpotential of potentially existed impurities oxides in A~D

	$\triangle G_{O^*}$	$\triangle G_{OH}^*$	$\triangle G_{OOH}^*$	$\triangle G_1$	$\triangle G_2$	$\triangle G_3$	$\triangle G_4$	η_{OER} (mV)
CaO_2 (1 1 0)	3.28	0.95	4.24	0.95	2.33	0.96	0.68	1103
$CaRuO_3$ (1 1 0)	-1.42	-2.79	-3.71	-2.79	1.36	-2.29	8.63	7401
Mn_2O_3 (1 1 0)	1.13	0.17	1.81	0.17	0.96	0.68	3.11	1881
Mn_3O_4 (3 1 1)	-1.74	0.76	-1.33	0.76	-2.50	0.42	6.25	5018
MnO_2 (1 1 1)	-0.42	-1.09	1.46	-1.09	0.67	1.88	3.46	2227
Nd_2O_3 (1 0 1)	40.83	-1.99	1.26	-1.99	42.81	-39.57	3.66	41581
PrO (1 1 1)	-2.84	-2.53	-5.57	-2.53	-0.31	-2.73	10.49	9260
Sr_3CaO_4 (1 1 1)	3.31	1.48	4.06	1.48	1.83	0.76	0.86	600
Sr_3CaO_4 (2 0 0)	2.40	2.08	4.77	2.08	0.32	2.37	0.15	1141
$SrCa_3O_4$ (1 1 1)	-4.66	0.56	0.70	0.56	-5.21	5.36	4.22	4125
$SrCa_3O_4$ (2 0 0)	4.56	2.22	4.85	2.22	2.34	0.29	0.07	1110
$SrCaO_2$ (1 1 1)	3.33	0.81	4.64	0.81	2.52	1.31	0.28	1294
$SrCaO_2$ (2 0 0)	3.50	0.95	4.14	0.95	2.55	0.64	0.78	1319
SrO_2 (1 1 0)	-0.59	1.85	0.93	1.85	-2.45	1.52	3.99	2762
$SrRuO_3$ (1 2 1)	-1.26	-1.28	-1.72	-1.28	0.02	-0.46	6.64	5406

Supplementary Note 6 References:

1. I. C. Man *et al.*, Universality in oxygen evolution electrocatalysis on oxide surfaces. *Chemcatchem* **3**, 1159-1165 (2011).
2. E. Musa, F. Doherty, B. R. Goldsmith, Accelerating the structure search of catalysts with machine learning. *Current Opinion in Chemical Engineering* **35**, 100771 (2022).
3. R. Ding, X. Wang, A. Tan, J. Li, J. Liu, Unlocking New Insights for Electrocatalyst Design: A Unique Data Science Workflow Leveraging Internet-Sourced Big Data. *ACS Catalysis* **13**, 13267-13281 (2023).
4. G. T. K. K. Gunasooriya, J. K. Nørskov, Analysis of Acid-Stable and Active Oxides for the Oxygen Evolution Reaction. *ACS Energy Letters* **5**, 3778-3787 (2020).
5. S. Back, K. Tran, Z. W. Ulissi, Toward a Design of Active Oxygen Evolution Catalysts: Insights from Automated Density Functional Theory Calculations and Machine Learning. *ACS Catalysis* **9**, 7651-7659 (2019).
6. Y. Jiao, Y. Zheng, M. Jaroniec, S. Z. Qiao, Design of electrocatalysts for oxygen- and hydrogen-involving energy conversion reactions. *Chem Soc Rev* **44**, 2060-2086 (2015).
7. S. Chen *et al.*, Mn-Doped RuO2 Nanocrystals as Highly Active Electrocatalysts for Enhanced Oxygen Evolution in Acidic Media. *ACS Catalysis* **10**, 1152-1160 (2019).
8. L. Li *et al.*, Spin-Polarization Strategy for Enhanced Acidic Oxygen Evolution Activity. *Adv Mater* **35**, e2302966 (2023).
9. Y. Gu *et al.*, Crystal Splintering of β-MnO2 Induced by Interstitial Ru Doping Toward Reversible Oxygen Conversion. *Chemistry of Materials* **33**, 4135-4145 (2021).
10. L. Qiu, G. Zheng, Y. He, L. Lei, X. Zhang, Ultra-small Sn-RuO2 nanoparticles supported on N-doped carbon polyhedra for highly active and durable oxygen evolution reaction in acidic media. *Chemical Engineering Journal* **409**, (2021).
11. Y. Wang *et al.*, Unraveling oxygen vacancy site mechanism of Rh-doped RuO(2) catalyst for long-lasting acidic water oxidation. *Nat Commun* **14**, 1412 (2023).
12. R. Ovcharenko, E. Voloshina, J. Sauer, Water adsorption and O-defect formation on Fe(2)O(3)(0001) surfaces. *Phys Chem Chem Phys* **18**, 25560-25568 (2016).
13. S. Goverapet Srinivasan *et al.*, A comparative study of surface energies and water adsorption on Ce-bastnasite, La-bastnasite, and calcite via density functional theory and water adsorption calorimetry. *Phys Chem Chem Phys* **19**, 7820-7832 (2017).
14. R. R. Rao *et al.*, Surface Orientation Dependent Water Dissociation on Rutile Ruthenium Dioxide. *The Journal of Physical Chemistry C* **122**, 17802-17811 (2018).
15. J. Greeley, J. K. Nørskov, Electrochemical dissolution of surface alloys in acids: Thermodynamic trends from first-principles calculations. *Electrochimica Acta* **52**, 5829-5836 (2007).
16. M. Umer *et al.*, Machine learning assisted high-throughput screening of transition metal single atom based superb hydrogen evolution electrocatalysts. *Journal of Materials Chemistry A* **10**, 6679-6689 (2022).
17. M. Ha *et al.*, Tuning metal single atoms embedded in NxCy moieties toward high-performance electrocatalysis. *Energy & Environmental Science* **14**, 3455-3468 (2021).
18. S. Hao *et al.*, Dopants fixation of Ruthenium for boosting acidic oxygen evolution stability and activity. *Nat Commun* **11**, 5368 (2020).
19. A. Li *et al.*, Enhancing the stability of cobalt spinel oxide towards sustainable oxygen evolution in acid. *Nature Catalysis* **5**, 109-118 (2022).
20. H.-Y. Su, K. Sun, DFT study of the stability of oxygen vacancy in cubic ABO3 perovskites. *Journal of Materials Science* **50**, 1701-1709 (2014).
21. X. Duan *et al.*, Cobalt-Doping Stabilized Active and Durable Sub-2 nm Pt Nanoclusters for Low-Pt-Loading PEMFC Cathode. *Advanced Energy Materials* **12**, (2022).
22. I. C. Man *et al.*, Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces. *ChemCatChem* **3**, 1159-1165 (2011).

23.   T. Reier, H. N. Nong, D. Teschner, R. Schlögl, P. Strasser, Electrocatalytic oxygen evolution reaction in acidic environments–reaction mechanisms and catalysts. *Advanced Energy Materials* **7**, 1601275 (2017).

24.   J. Gao, H. Tao, B. Liu, Progress of Nonprecious-Metal-Based Electrocatalysts for Oxygen Evolution in Acidic Media. *Adv Mater* **33**, e2003786 (2021).