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Prediction of Stable and Active (Oxy-Hydro) Oxide Nanoislands on Noble-Metal Supports for Electrochemical Oxygen Reduction Reaction

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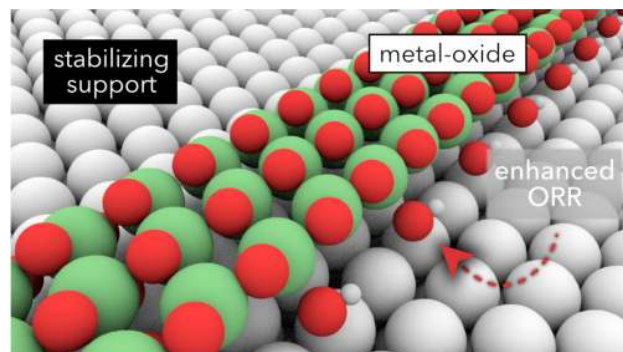
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ABSTRACT: Developing cost-effective oxygen electrocatalysts with high activity and stability is key to their commercialization. However, economical earth-abundant catalysts based on first-row transition-metal oxides suffer from low electrochemical stability, which is difficult to improve without compromising their activity. Here, using density functional theory calculations, we demonstrate that noble-metal supports lead to bifunctional enhancement of both the stability and the oxygen reduction reaction (ORR) activity of metal (oxy-hydro) oxide nanoislands. We observe a significant stabilization of supported nanoislands beyond the intrinsic stability limits of bulk phases, which originates from a favorable lattice mismatch and reductive charge transfer from oxophilic supports. We discover that interfacial active sites (located between the nanoisland and the support) reinforce the binding strength of reaction intermediates, hence boosting ORR activity. Considering both stability and activity lead to discovery of CoOOH|Pt, NiOOH|Ag, and FeO₂|Ag as viable systems for alkaline ORR, we then use a multivariate linear regression method to identify elementary descriptors for efficient screening of promising cost-effective nanoisland|support catalysts.

KEYWORDS: *oxide, oxy-hydroxide, FCC metal supports, density functional theory calculations, oxygen reduction reaction, Pourbaix diagrams, correlation analysis, multivariate linear regression*



INTRODUCTION

The development of new active, stable, and cost-effective alternative catalysts has been of utmost focus in renewable and sustainable future energy technologies such as fuel cells, electrolyzers, and metal–air batteries.^{1–4} In fuel cell cathodes,^{2,5} in particular, innovative materials to replace the state-of-the-art Pt-based catalysts would benefit automotive and stationary applications.^{6–8} Although various successful approaches to increase catalytic activities and reduce Pt dependency have been proposed, achieving both high activity and stability simultaneously turned out to be challenging without sacrificing other properties.^{2–4,6–8} Therefore, new design principles to improve activity and stability, combined with a theoretical platform that is readily applicable to other catalyst systems or electrochemical reactions are essential.

First-row transition-metal materials have been targeted for various electrochemical reactions because of their abundance,

high activity, and tunable morphology.^{9–13} Their (oxy-hydro) oxides have largely been explored as alkaline oxygen evolution reaction (OER) catalysts, whereas their oxygen reduction reaction (ORR) performances have not been studied thoroughly.^{14,15} Recently, various approaches such as core–shell morphology,^{16–18} nanostructuring,^{19–21} single-atom catalysts,^{22,23} introduction of atomic defects,²⁴ or coupling with support materials^{9,25–27} have been suggested to enhance the intrinsic catalytic activities. Such modified Mn–Co-based oxides were reported as promising alkaline ORR and OER catalysts^{24–26,28} with activities close to the state-of-the-art Pt and Ir metals. Recently, Zhao et al. reported systematic theoretical results on the ORR/OER activity of layered 3d

transition-metal oxides, oxy-hydroxides, and hydroxides, with several candidates predicted to be active toward ORR and OER.¹²

Noble-metal supports can significantly modify thermodynamic properties of several types of ultrathin oxide films compared to their bulk counterparts.²⁹ Furthermore, density functional theory (DFT) calculations predicted that the film–support–electrolyte three-phase boundary promotes kinetics of alkaline hydrogen evolution reaction, later also confirmed by experiments.^{30–33} The beneficial role of Au support was also demonstrated for alkaline OER, with improvement reported for thin CoO_x ,²⁷ NiO_x ,³⁴ CoCeO_x ,³⁵ NiCeO_x ,⁹ and core–shell CoFeO_x .¹⁸ Recent emergence of single-layer cobalt oxide nanoislands supported on gold³⁵ established H_2O catalytic reactivity at the edges of the nanoislands.³⁶ Therefore, combined experimental and theoretical results indicate that the stability as well as the activity can be tuned by changing the support materials, prompting a comparative study on the support effects. However, to our knowledge, there has been no theoretical study on the application of supported (oxy-hydro) oxide systems for ORR due to the added computational complexity of extended systems consisting of magnetic metal oxides.

Here, we systematically investigate (oxy-hydro) oxide nanoislands supported on metals using DFT calculations to study the bifunctional effect of supports on the stability and ORR activity of nanoislands. We construct Pourbaix diagrams of the nanoisland/support– H_2O systems to predict their stability under the ORR conditions, evaluate their ORR activity, and discover novel stable and active candidates. In addition, we also perform a correlation analysis to select features of the atomic structure that significantly affect the stability and activity, and propose descriptors through a multivariate linear regression to predict the target properties from readily available quantities.

RESULTS

Trends in Stabilization Effects of Support Metals.

Zeng et al. first demonstrated that the support can significantly stabilize the (oxy-hydro) oxides.²⁹ Here, four metal oxides (MO_2 , $M = \text{Co}, \text{Fe}, \text{Mn}, \text{Ni}$) and metal oxy-hydroxides (MOOH) in the form of single-layer nanoribbons are supported on three face-centered cubic (FCC) metal supports (Ag, Au, and Pt) (Figure 1).^{35,37,38} In all cases, we observed less than 10% of lattice mismatches between nanoribbons and supports (see Supporting Information, Table S1) which leads to commensurate lattice matching along the $[110]$ direction (Figure 1). We selected the most stable $Z(111)$ -type edge termination for the nanoribbon with the width of three oxide units separated by three FCC metal layers.³⁷ As a result, the (2×3) nanoribbon is placed onto (2×6) FCC support denoted, hereafter, as nanoisland/support. For simplicity, we assume only 0% (Figure 1a) and 100% hydroxylation (Figure 1b), while experimentally intermediate levels of hydroxylation are possible.^{35,37,38}

To understand the trends of support effects on stabilizing nanoislands, we evaluate the interface formation energy as²⁹

$$E_{\text{interface}} = [E_{\text{MO}_2\text{H}_x+\text{FCC}} - E_{\text{FCC}} - nE_{\text{MO}_2\text{H}_x}]/n \quad (1)$$

where $E_{\text{MO}_2\text{H}_x+\text{FCC}}$, E_{FCC} , and $E_{\text{MO}_2\text{H}_x}$ are electronic energies of the total system, metal support, and bulk (oxy-hydro) oxide, and n is the number of oxide units in the nanoisland. To

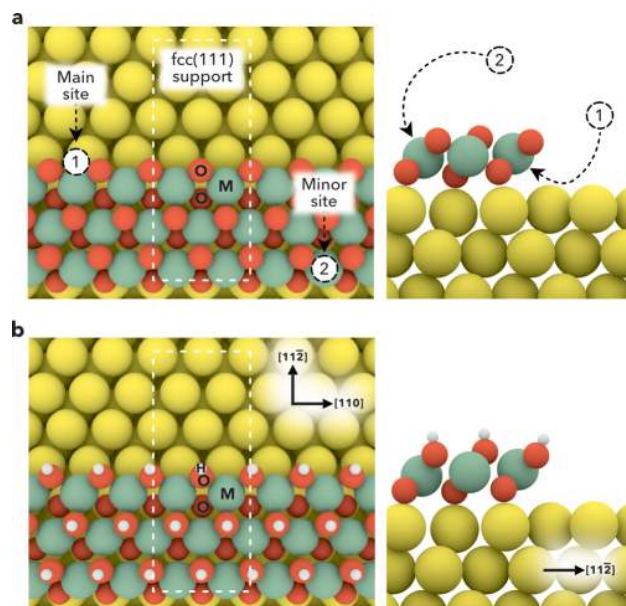


Figure 1. Geometries of nanoisland/support systems. Top and side views of (a) oxide/support and (b) oxy-hydroxide/support. Interfacial main site (1), where adsorbates interact with both support and nanoislands directly, and stand-alone minor site (2), where adsorbates only interact with nanoislands are indicated. Color code: support metals (yellow), nanoisland metals (green), oxygens (red), and hydrogens (white).

calculate bulk electronic energies, we assumed the layered structures to be the most stable for Fe and Mn (oxy-hydro) oxides, although goethite FeOOH ³⁹ and pyrolusite MnO_2 ⁴⁰ are slightly more stable than the layered polymorph by a few meV per formula unit (f.u.).^{39,41,42} Importantly, Co and Ni (oxy-hydro) oxides readily form stable layered structures.

In Figure 2a, we present the calculated $E_{\text{interface}}$ for all nanoisland/support systems as a function of supports. Because the $E_{\text{interface}}$ is referenced to the bulk energy of (oxy-hydro) oxides, this quantity is a measure of (de)stabilization of the nanoislands in the presence of support. Generally, we found that the stabilization effects increase as the support changes from Au to Ag and to Pt. This finding can be directly linked to oxophilicity of the support metals because of chemical interactions between oxygen atoms in nanoislands and the metal supports. In addition, analysis of the projected density of states of nanoisland/support shows that the d-band of the support metal is shifted toward the Fermi level as the support changes from Ag to Au to Pt, indicating stronger electronic interactions with nanoislands (Figure S1). Oxides (open symbols) are always more stabilized than oxy-hydroxides (closed symbols), NiOOH being the only exception. The reason behind this trend is simply because highly oxidized MO_2 oxides are much less stable their MOOH counterparts. On the other hand, the reason for the exception is that NiOOH tends to be significantly reduced compared to other MOOH . Specifically, the oxidation states of Ni metals in NiOOH on all supports were found to be 2+, while the oxidation states of other MOOH are combinations of 2+ and 3+ (Table S3). Because NiOOH is exceptionally more reduced, the stabilization trend of $\text{NiO}_2/\text{NiOOH}$ is different from other MO_2/MOOH . Remarkably, we notice an almost constant gap between the $E_{\text{interface}}$ energies of oxides and oxy-

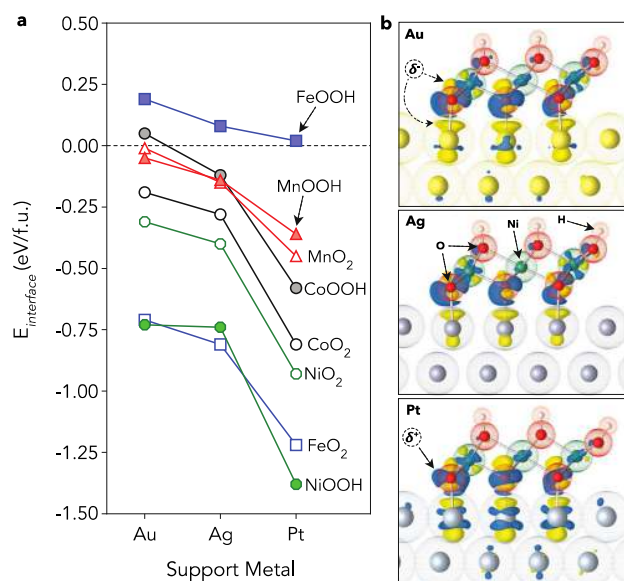


Figure 2. Support effects on the stabilization of nanoislands. (a) Calculated interface formation energy ($E_{\text{interface}}$) of nanoisland/support systems. (b) Isostructural charge density difference plots of the NiOOH/supports. The isosurface level is $\delta = \pm 0.005 \text{ e}/\text{\AA}^3$. Yellow (blue) represents charge depletion (accumulation). The dotted spheres represent ionic radii.

hydroxides independently of a metal support (Figure S2). Maintaining the MO_2/MOOH equilibrium potential at a

nearly constant level has major implications on ORR stability as will be discussed below.

To understand electronic interactions between the nanoislands and the supports, we have performed Bader charge analysis and presented the isostructural charge density difference of NiOOH/support systems upon adsorption. We have found that in all cases, metal support donates electrons to the nanoislands and the amount of the electron transfer is proportional to stabilization of the interface (Figure S3a). A visualization of reductive charge transfer evidenced that oxygen and metal atoms of the nanoislands gain electrons from supports (Figure 2b). We note that the oxidizing effect of the supports in supported double layer (MO) with reverse O–M binding geometry was determined by the electronegativity difference of facing metals.¹³ In our case, the metal supports bind to metal oxide via oxygens which have significantly higher electronegativity than transition metals.

To obtain quantitative insights on the reduction effects of the supports, we have analyzed the change in the local magnetic moment (μ_B) of the transition metals in the nanoislands relative to values of their bulk metal (oxy-hydro) oxides (Table S3).^{9,10,43} For example, bulk calculations of Co +2, +3, and +4 in $\text{Co}(\text{OH})_2$, CoOOH , and CoO_2 at the PBE + U level of DFT assign the μ_B of the Co atom to be 2.75 (high-spin), 0 (low-spin), and 1.18 (low-spin), respectively, which allows to indirectly identify the oxidation state of the metal. The calculated μ_B of 2/3 Co atoms in CoOOH/Ag is ~ 2.6 , and μ_B of 1/3 Co atoms is 0.0, which correspond to +2 and +3, respectively, resulting in a net oxidation state of +2.33. On the other hand, μ_B of all Co atoms in CoOOH/Pt is ~ 2.6 ,

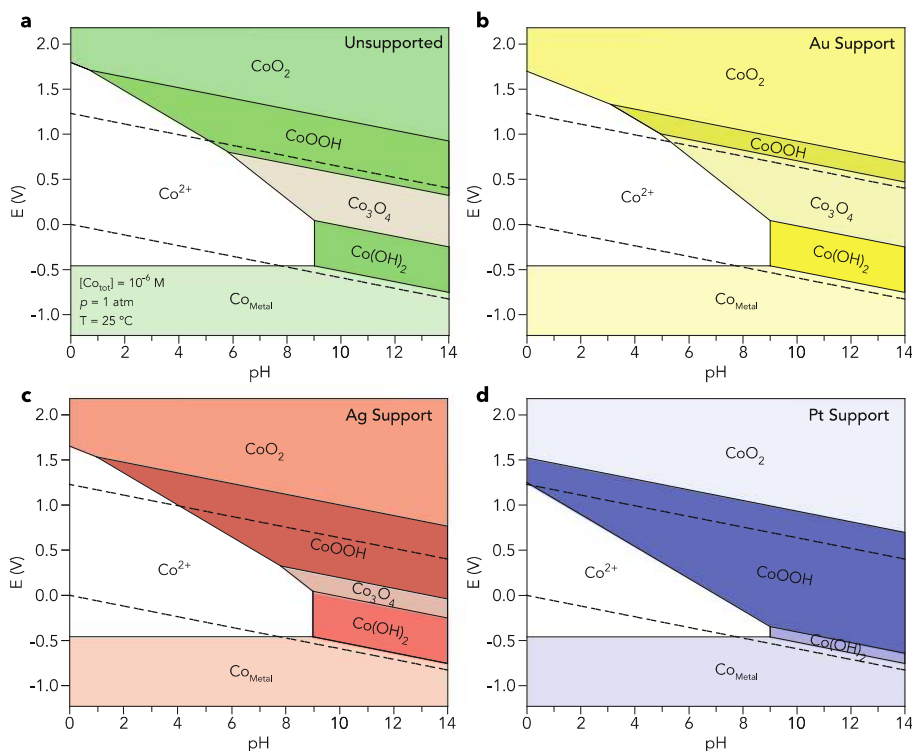


Figure 3. Pourbaix diagrams of (un)supported Co–H₂O phases. Diagrams of (a) unsupported, (b) Au-supported, (c) Ag-supported, and (d) Pt-supported $\text{CoO}_2/\text{CoOOH}$. The unsupported plot (a) is based on the experimental values of formation free energies of bulk phases (Table S2), and calculated $E_{\text{interface}}$ of CoO_2 and CoOOH were added for each support (from Figure 2a) to construct (b–d). Dashed lines are the equilibrium potentials for oxygen ($E_{\text{O}_2/\text{H}_2\text{O}} = 1.23 \text{ V}_{\text{RHE}}$) and hydrogen ($E_{\text{H}^+/\text{H}_2} = 0.00 \text{ V}_{\text{RHE}}$) electrochemistry.

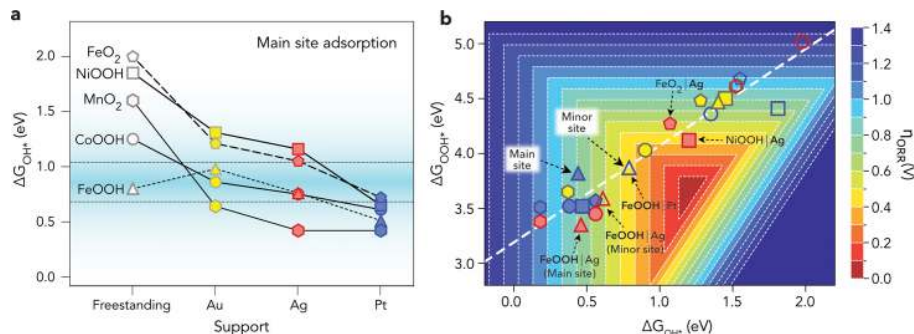


Figure 4. Support effects on the ORR activities. (a) Main-site OH^* binding free energy, ΔG_{OH^*} . The range of optimal ΔG_{OH^*} is highlighted in blue.² The results for unsupported nanoislands are taken from ref 12. (b) Two-dimensional ORR volcano plot of examined nanoisland/support systems plotted as a heat map of calculated η_{ORR} vs ΔG_{OH^*} and ΔG_{OOH^*} . Same colors and markers referring to the atomic structures are used for (a,b). Full and empty symbols correspond to adsorptions at the main site and minor site, respectively. The white dashed line shows a correlation between ΔG_{OH^*} and ΔG_{OOH^*} ($\Delta G_{\text{OOH}^*} = 0.88\Delta G_{\text{OH}^*} + 3.19$ eV).

indicating that all Co +3 atoms are reduced to +2, confirming the electron transfer from the support to the nanoislands. Comparing the oxidation states of Co in CoOOH on Ag, Au, and Pt as explained above, we have therefore identified that the reducing ability of Ag and Au is similar, whereas that of Pt is comparatively stronger.

Electrochemical Stability Enhancement beyond the Bulk Limits. To investigate the stability of the nanoislands under relevant ORR conditions, we have constructed Pourbaix diagrams of the nanoisland/support systems (Figures 3 and S4–S6) by incorporating the effects of noble-metal supports ($E_{\text{interface}}$) into the unsupported bulk Pourbaix diagram. From this analysis, we confirm that the difference in $E_{\text{interface}}$ is support-insensitive (Figures 3 and S2), that is, the MO_2/MOOH equilibrium potential of $M = \text{Co}, \text{Ni},$ and Mn for all supports is roughly 1.5, 1.3, and 0.8 V_{RHE} , respectively. Because oxides (MO_2) are the most stable phase above the equilibrium potential, we predict CoO_2 and NiO_2 phases to be irrelevant under ORR conditions (operating potential near 0.8 V_{RHE} ¹⁷). On the other hand, the FeO_2 region dominates and FeOOH disappears from the Pourbaix diagram on all the metal supports because of significant support-induced stabilization (Figure S4).

The analysis of the Pourbaix diagrams of the nanoisland/support composites allows us to determine the relevant phase to the targeted electrochemical reaction. For instance, the most stable phase of Co nanoislands on Ag and Pt supports under the ORR condition ($\sim 0.8 V_{\text{RHE}}$) is CoOOH because of the stabilization effects of the support metals (-0.12 and -0.58 eV/f.u., respectively), while CoOOH on Au is destabilized by 0.05 eV/f.u., making Co_3O_4 most stable at ORR potentials. The ORR activities of related phases determined from the Pourbaix analysis are discussed below.

Activity Enhancement of Nanoisland/Support Systems. The effective ORR activity of the nanoisland/support systems can be evaluated from the thermodynamics of the associative reaction mechanism^{2,44} (see the Methods section for details). Such MO_2 and MOOH nanoislands feature two types of edge sites. First, there is a unique main site (labeled as (1) in Figure 1) with adsorbates in direct contact with the nanoisland and the support, and where large synergistic interfacial effect is expected.^{9,45} Then, there is a stand-alone minor site (labeled as (2) in Figure 1), which is not in contact with the support and only indirect interactions are expected. For the materials that bind too strongly at the main site, we

have subsequently explored binding at the minor site. During the electrochemical process, the O^* or OH^* coverage of active sites is a function of an applied potential and was determined via the surface Pourbaix diagram analysis (Figures S7 and S8). All adsorption geometries and associated energies are available online,⁴⁶ and two examples are illustrated in Figures S9 and S10.

The most important descriptor for the ORR activity is the free energy of OH^* binding ΔG_{OH^*} .² We have plotted ΔG_{OH^*} of main site adsorption for the studied noble-metal supports in Figure 4a, and for comparison, we have also included the results for unsupported single-layer (oxy-hydro) oxides from our recent study.¹² We observe that OH^* binding at all nanoisland/support systems is stronger than at unsupported systems (FeOOH being the only exception), demonstrating the positive effect of support on the adsorbates at the interfacial main site. Similar to the stabilization trend, we observed gradual strengthening of the OH^* adsorption as the support material changes from Au to Ag to Pt in all cases. Therefore, as discussed above, the activity trends could also be correlated with the oxygen affinity of the support metals because OH^* interacts directly with the nanoisland and the metal support (Figure S9). We note that ΔG_{OH^*} of unsupported FeOOH is stronger than that of FeOOH/Au and FeOOH/Ag , where this exceptional behavior could be originated from the destabilization of FeOOH on Ag and Au (Figure 2a). For nanoisland/support systems with too strong ΔG_{OH^*} at the main site ($\Delta G_{\text{OH}^*} < 0.8$ eV), we have additionally considered the minor site as active sites (hollow symbols in Figure 4b). We note that ΔG_{OH^*} is less correlated with the amount of transferred electrons (Figure S3b), unlike the stabilization of the interface, which is strongly correlated with the amount of transferred electrons. A possible reason behind this observation is that adsorbates interact directly with both the metal support and nanoisland.

The ORR activities of the nanoisland/support systems for both the main site and minor site are summarized in Figure 4b. This plot shows the two-dimensional volcano plot which predicts theoretical ORR overpotential, η_{ORR} (see the Methods section), based on ΔG_{OH^*} and ΔG_{OOH^*} energies and $\Delta G_{\text{O}^*} = 2\Delta G_{\text{OH}^*}$ scaling.² The scaling relation for the main-site adsorption of nanoisland/support (white dashed line, $\Delta G_{\text{OOH}^*} = 0.88\Delta G_{\text{OH}^*} + 3.19$) was found to be very similar to the previously reported universal scaling relation for various classes of materials ($\Delta G_{\text{OOH}^*} = \Delta G_{\text{OH}^*} + 3.2$).^{2,14} On the basis

of this analysis, we discover CoOOH|Au, NiOOH|Ag, and FeO₂|Ag as the active catalyst systems for the ORR with a η_{ORR} of 0.34, 0.43, and 0.58 V, respectively. For the minor-site binding, we find that CoOOH|Pt and FeOOH|Pt to be active with a η_{ORR} of 0.67 and 0.59 V, respectively. However, taking stability requirements into consideration, the most promising candidates for alkaline ORR catalysts are NiOOH|Ag, FeO₂|Ag, and CoOOH|Pt (see Figures 3b and S4–S6). We note that all these candidates are predicted to be as active as the Pt catalyst with an overpotential (η_{ORR}) of ~ 0.50 V.¹⁷ Additionally, we have checked the existence of favorable sites, where the dissociative mechanism could play a role. Using the results for unsupported metal oxides,¹² only the exposed metal-edge bridge sites of NiOOH have sufficiently low vacancy formation energy to be similar in activity to main and minor sites in the associative mechanism.

Prediction of Activity and Stability Descriptors. For future rational design of nanoisland|support catalysts, it is beneficial to find elementary descriptors that predict our target properties, ΔG_{OH^*} for activity and $E_{\text{interface}}$ for stability, without a need for expensive DFT calculations required for such extended nanostructured systems. In this sense, we have identified various features (Table 1) that are easily available

Table 1. Features of the Nanoisland|Support Systems

abbreviation	description
$q_{\text{M,free}}$	Bader charge of the active metal atom of freestanding (oxy-hydro) oxides ¹²
$\Delta G_{\text{OH}^*,\text{free}}$	OH* binding free energy of freestanding (oxy-hydro) oxides ¹²
d_{M}	the number of d electrons of the metal in nanoislands from a formal oxidation state
χ_{M}	electronegativity of the metal in nanoislands
$q_{\text{M,S}}$	Bader charge of the main-site metal atom in nanoislands of nanoisland support systems
d_{S}	the number of d electrons of support metals
χ_{S}	electronegativity of support metals
$\Delta G_{\text{OH}^*,\text{S}}$	OH* binding free energy on the (111) surface of support metals
q_{S}	Bader charge of support metals in nanoisland support systems

and already reported in the literature, and plotted their relative correlation with our target properties. Figure 5a shows that the electronegativity of the metal in nanoislands (χ_{M}) and OH* binding free energy of support metals ($\Delta G_{\text{OH}^*,\text{S}}$) are the two most correlated features with ΔG_{OH^*} at the main site, while OH* binding free energy of freestanding nanoislands ($\Delta G_{\text{OH}^*,\text{free}}$) and Bader charge of support metals (q_{S}) are the two most correlated features with $E_{\text{interface}}$. Therefore, we used χ_{M} and $\Delta G_{\text{OH}^*,\text{S}}$ to fit the linear model for ΔG_{OH^*} . In the latter case, however, we used $\Delta G_{\text{OH}^*,\text{S}}$, instead of q_{S} , because using both $\Delta G_{\text{OH}^*,\text{free}}$ and q_{S} is redundant as they are highly correlated with each other ($R^2 \geq 0.80$, see Figure 5b). The resulting linear models

$$\Delta G_{\text{OH}^*}(\text{lin. reg.}) = -4.32 + 1.87\chi_{\text{M}} + 1.14\Delta G_{\text{OH}^*,\text{S}} \quad (2a)$$

$$E_{\text{interface}}(\text{lin. reg.}) = -0.30 - 0.88\Delta G_{\text{OH}^*,\text{free}} + 0.81\Delta G_{\text{OH}^*,\text{S}} \quad (2b)$$

present simple but effective descriptors to predict ΔG_{OH^*} and $E_{\text{interface}}$ of the nanoisland|support systems, respectively. Figure 5c,d shows that such descriptors could reasonably predict the

target values within a mean absolute error of 0.20 eV using only two features in both cases. Notably, $\Delta G_{\text{OH}^*,\text{S}}$ plays a significant role in determining both target values, further underlying the bifunctionality of the noble-metal supports on the activity and selectivity, as discussed above.

Lastly, it is convenient that $\Delta G_{\text{OH}^*,\text{S}}$ is readily available from simple binding energy calculations, which is significantly more cost-effective than the current DFT calculations of extended nanoisland|support systems, and χ_{M} and $\Delta G_{\text{OH}^*,\text{free}}$ are already tabulated and available online at Catalysis-hub.org.¹² Our analysis provides a practical and useful approach to screen new combinations of nanoisland|support systems for ORR without expensive DFT calculations. For instance, for highly oxygen-affinitive FCC metals (Cu, Ni, Rh), our model predicts significant stabilization of the nanoislands and strengthening of the main-site OH* binding (Table S4), suggesting that Cu, Ni, and Rh are not appropriate metal supports of nanoislands for ORR due to too strong OH* binding.

CONCLUSIONS

The bifunctional effect of noble-metal supports on stabilizing (oxy-hydro) oxide nanoislands and hence enhancing ORR activity were demonstrated by using DFT calculations. The stabilization effects introduce new composite phases beyond the intrinsic stability limits of bulk phases. The unique interfacial active sites between supports and nanoislands enhance the binding strength of oxygenated species compared to their unsupported counterparts, discovering CoOOH|Pt, NiOOH|Ag, and FeO₂|Ag to be active and stable catalysts for alkaline ORR. To generalize such support effects, we have developed predictive descriptors using multivariate linear regression. The combined correlation and linear regression analysis reinforces the finding that oxygen affinity of the support metal plays a key role for both activity and stability. These results provide a theoretical framework for prediction of essential properties of the future nanoisland|support catalysts.

METHODS

Computational Parameters. All electronic structure calculations were performed within GGA-PBE⁴⁷ plus Hubbard-U framework (PBE + U) using projector-augmented wave pseudopotentials^{48,49} as implemented in the VASP code.^{50,51} The Hubbard effective terms $U_{\text{eff}}(\text{Co}) = 3.32$ eV, $U_{\text{eff}}(\text{Fe}) = 5.3$ eV, $U_{\text{eff}}(\text{Mn}) = 3.9$ eV, and $U_{\text{eff}}(\text{Ni}) = 6.2$ eV were chosen from the Materials Project database^{52,53} and added to the PBE exchange–correlation functional as proposed by Dudarev et al.⁵⁴

Spin-polarized DFT calculations were performed, and the most stable magnetic structures between ferromagnetic and antiferromagnetic were considered. The plane wave energy cutoff was set to 500 eV, and 15 Å of vacuum was added in the z-direction to avoid undesirable interaction between repeating images. All structures contain the (2 × 3) supercell of the MO₂/MOOH monolayer (M = Co, Fe, Mn, Ni) supported on the (2 × 6) supercell of metals (Ag, Au, Pt) with the bottom two layers fixed to the bulk positions (Figure 1). All structures are sampled by the (4 × 1 × 1) Monkhorst–Pack k-point mesh.⁵⁵ The convergence criteria for energy (self-consistent iteration) and force (ionic relaxation) were set to be 10^{−4} eV and 0.05 eV/Å, respectively.

Between the associative^{2,44} and dissociative^{44,56} ORR mechanisms, we have only considered the associative reaction mechanism to investigate the ORR catalytic activity of nanoisland|support systems. The dissociative mechanism affects only the weakly binding active sites ($\Delta G_{\text{OH}^*} > 0.92$ eV), and in principle can improve the limitations of OOH* formation of the associative mechanism, provided that sites

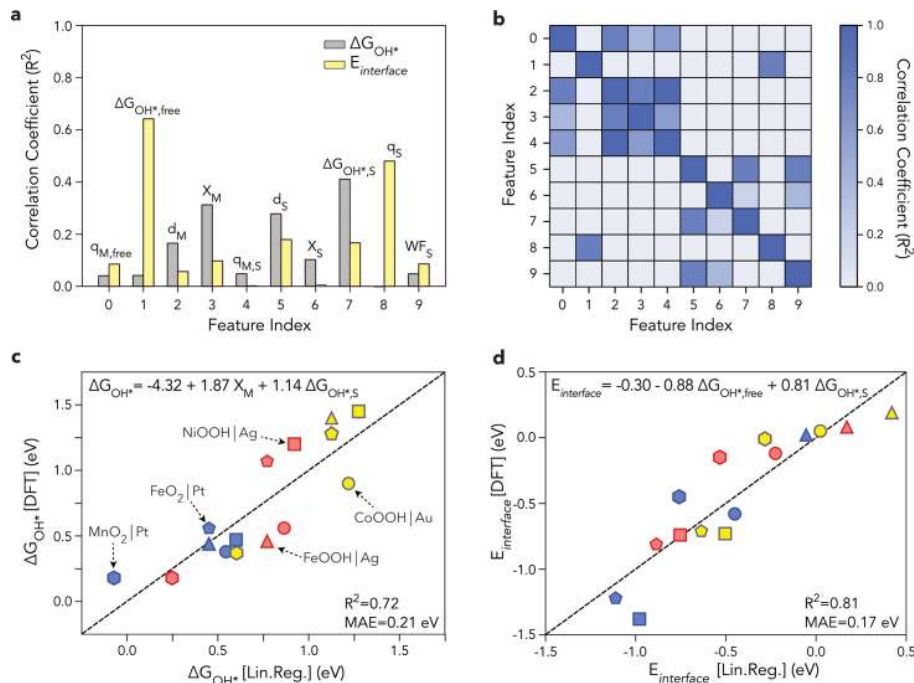
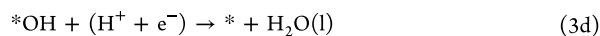
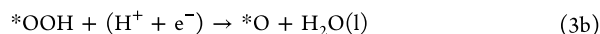
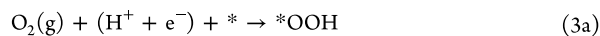


Figure 5. Multivariate linear regression analysis. (a) Correlation coefficient (R^2) of each feature toward the target properties, ΔG_{OH^*} and $E_{\text{interface}}$. (b) Correlation coefficient matrix between the features. Darker color indicates higher correlation between two individual features. Comparison between predicted values from descriptors and calculated values from DFT for (c) ΔG_{OH^*} and (d) $E_{\text{interface}}$ with symbols defined in Figure 4.

with favorable oxygen vacancy do exist. The associative mechanism is as follows:



The calculated electronic energies were converted into free energies by including free energy corrections for adsorbates and gaseous molecules (Tables S5 and S6). We then used the computational hydrogen electrode method⁴⁴ to take into account the effect of the applied potential on free energy changes, where the chemical potential of the proton–electron pair is set to be equivalent to that of gas-phase H_2 in the standard condition, $[\mu(\text{H}^+ + \text{e}^-) = 1/2\mu(\text{H}_2)]$. As the potential U_{elec} versus the reversible hydrogen electrode (RHE) is applied, the chemical potential of the electron is shifted by $-eU_{\text{elec}}$ thus, $[\mu(\text{H}^+ + \text{e}^-) = 1/2\mu(\text{H}_2) - eU_{\text{elec}}]$. Then, the ORR catalytic activity is determined based on ORR overpotential (η_{ORR}), where $\eta_{\text{ORR}} = \max[\Delta G_{2\text{a}}, \Delta G_{2\text{b}}, \Delta G_{2\text{c}}, \Delta G_{2\text{d}}]_{@U=1.23\text{V}}$.² Additional calculation details can be found in the Supporting Information.

Descriptor Exploration. We selected features from a correlation analysis, where we evaluated all pair-wise correlations between a set of features of the atomic models, as well as correlations with the target values, ΔG_{OH^*} and $E_{\text{interface}}$. We then utilized Scikit-learn, a Python-based machine learning library⁵⁷ to fit a multivariate linear regression model in several dimensions to compare the correlation of DFT calculation resulting with physical properties of the system listed in Table 1.

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Notes

The authors declare no competing financial interest.

All calculated structures with associated adsorption energies are available to download at Catalysis-hub.org.^{12,46} The Jupiter notebook for the linear regression model will be provided upon request to corresponding authors.

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