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Dual-site OER Mechanism Exploration Through Regulating the Asymmetric Multi-site NiOOH

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Abstract:

Asymmetric Nickel oxyhydroxide (NiOOH) possesses multi-OH and O active sites on different surfaces (001) and (00\textbar 1), which possibly causes complicated catalytic process. The density functional theory (DFT) calculations reveals that the unconventional dual-site mechanism (UDSM) of oxygen evolution reaction (OER) on NiOOH (001) on (00\textbar 1) exhibits significantly lower overpotentials of 0.80 and 0.77 \textit{V} than 1.24 and 1.62 \textit{V} for single-site mechanism (SSM), respectively. Through chemical doping or heterojunction modifications, the constructed NiOOH@FeOOH (00\textbar 1) heterojunction reduces the thermodynamic overpotential to 0.49 \textit{V} from the original 0.77 \textit{V} undergoing UDSM. Although Fe/Co-doping or physical compression yield similar or slightly higher overpotentials, and is not conductive to facilitate OER process along UDSM, all the dual-site paths exhibit obviously lower overpotentials than SSM for pristine and regulated NiOOH (001) and (00\textbar 1) from the whole viewpoint. This work identifies a more reasonable and efficient dual-site OER mechanism, which is expected to help the rational design of highly-efficient electrocatalysts.

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Introduction

Oxygen Evolution Reaction (OER) is the kinetically rate-limiting reaction on cathode in electrolysis, accompanied with the two-electron transfer anodic Hydrogen Evolution Reaction (HER).\textsuperscript{1,2} The water electrolysis in alkaline condition is one of the main approaches to produce hydrogen in industry, although the current is relatively low. The well-accepted four electron-proton transfer along the OER process is commonly regarded as evolution on single-site (SSM), especially for single-atom catalysts (SAC), via intermediates of OH*, O* and OOH*.\textsuperscript{3-6} However, this conventional four-step SSM mechanism obscures the reaction complexity occurrence on some electrocatalysts containing multi-active sites. Hence, several dual-site OER mechanisms have been proposed to more comprehensively understand the complex reaction on multi-sites and improve the design principles of OER catalysts.\textsuperscript{7}

The recent great progress was that the bifunctional mechanism has been validated by experimental detection of O*-O* intermediate. An unconventional bifunctional mechanism was proposed on A-M cooperative manner of two distinct metal sites A and M, where metal-M served as the OOH active center and metal-A acted as the H acceptor in Scheme 1a.\textsuperscript{8} Actually, the idea of multi-site reactivity for OER was firstly proposed by Wang \textit{et al.} in the study of oxygen vacant CoOOH. The H$^+$ transferred from the absorbed water to the adjacent Co$^{V}$, followed by a deprotonation step. DFT calculations further demonstrated the importance of dual-site reactivity by exploring the competitive OER mechanism-II and IV on $\beta$-CoOOH, corresponding to the intermediates B with dehydrogenating the neighbored OH and tetraoxidane species in scheme 1b.\textsuperscript{9} Another previously proposed dual site reaction is called conventional dual-site mechanism (CDSM) OER, involving the combination of two metal oxo species to form O-O step (Scheme 1c).\textsuperscript{8} The Similar dual-site reaction with two exposed oxygen atoms coupling to form O$_2$ has also been studied in an Iron Nickel Catalyst.\textsuperscript{10} Scheme 1d presents a different unconventional dual-site mechanism (UDSM) via O-H breakage to form OO*-OH* intermediate, which has been found to be more favorable than SSM mechanism based on the same material surface by our
The lattice oxygen in the structure of Bifunctional mechanism and CDSM is not involved in the reaction, however, it is involved in UII and UDSM, so it follows different reaction mechanisms in different surface states. UDSM has been demonstrated as a more favorite dual-site mechanism in our previous report on NiOOH@FeOOH due to lower overpotential of 0.76 V than 2.42 V undergoing the SSM. The advantage of dual-site is possibly ascribed to the synergy effects between two adjacent active sites to promote OER process.

Nickel oxyhydroxide (NiOOH) is one of the typical highly-active non-precious electrocatalysts containing multi-OH and O sites on different surfaces. β-NiOOH has hexagonal tightly stacked layered structure with smaller interlayer spacing, while γ-NiOOH belongs to the rhombic space with a larger interplanar spacing. β-NiOOH has been demonstrated to exhibit better OER performance than γ-NiOOH. The character of four different types of OH and O arrangements has been explored to evaluate the impact on structure stability and OER activity of β-NiOOH. The most stable structure was characterized to be a uniform H and OH alternative distribution with constructing Ni\(^{3+}\) ions of a half-occupied dz\(^2\) orbital. Two asymmetric edge β-

![Scheme](image-url)
NiOOH models was built to evaluate the OER catalytic performance by doping transition metals and combining with other hydroxide oxides.\textsuperscript{16–18} Our previous work combined with experimental measurement has explored dual-site mechanism called UDSM via O-H breakage with attaching on two active sites in FeOOH@NiOOH composites (Scheme 1d). The calculated thermodynamic overpotential along UDSM path was reduced to 0.76 V from 2.42 V of the traditional SSM mechanism.\textsuperscript{11} It found that UDSM mechanism on NiOOH surface is beneficial to improve OER performance.

In this work, we choose $\beta$-NiOOH with uniform Ni$^{3+}$ in two asymmetric O- and OH-terminations, to systematically investigate the dual-site mechanism feasibility by regulation of hybrid metal-doping, heterojunction composition and strain effect. Two asymmetric OH-terminated (001) and O-terminated (00\textsuperscript{1}) surfaces are evaluated the OER process under both the SSM and the unconventional dual-site mechanism (UDSM). Fe and Co doping effect are compared with FeOOH@NiOOH and CoOOH@NiOOH heteroconjuctions. We also explore the effect for OER activity of structure deformation by compressing along x and y axis. The various regulation on these two asymmetric surfaces are wholly compared to understand the modification on dual-site mechanism. The electronic variation on the active site of the various modification is analyzed to explore the inherent nature, which is expected to provide design principles for highly-efficient electrocatalyst.

**Computational Method**

**Computational Details**

All spin-polarized DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) based on the projector-augmented wave (PAW) method.\textsuperscript{19,20} The exchange–correlation energy was treated by the Perdew-Burke-Ernzerhof (PBE) functional at the generalized gradient approximation (GGA) level.\textsuperscript{21} A plane-wave basis set with the cut-off kinetic energy of 450 eV is employed to expand the smooth part of wave functions. The $k$-point meshes with a reciprocal space resolution of $2\pi \times 0.04$ Å\textsuperscript{-1} were utilized for structural optimization and static self-
consistent calculations, respectively. All atoms were allowed to relax until the Hellmann-Feynman forces were smaller than 0.03 eV/Å, and the convergence criterion for the electronic self-consistent loop was set to $10^{-4}$ eV. Brillouin zone is sampled with the $k$-point of $5 \times 5 \times 1$. To prevent interactions between periodic images, a vacuum space of 15 Å is utilized.

The reaction free energies of elementary step (1 ~ 4) are calculated with the computational hydrogen electrode (CHE) model proposed by Nørskov' group. Typical UDSM in OER process in alkaline environment can be described in the following step1~4. The process of SSM are provided in SI Methods.

### Step 1

\[ \text{O}^-\cdot\text{O}^- + \text{OH}^- \rightarrow \text{OO}^-\cdot\text{OH}^- + e^- \]

### Step 2

\[ \text{OO}^-\cdot\text{OH}^- + \text{OH}^- \rightarrow \text{HO}^-\cdot\text{OH}^- + \text{O}_2 + e^- \]

### Step 3

\[ \text{HO}^-\cdot\text{OH}^- + \text{OH}^- \rightarrow \text{O}^-\cdot\text{OH}^- + \text{H}_2\text{O} + e^- \]

### Step 4

\[ \text{O}^-\cdot\text{OH}^- + \text{OH}^- \rightarrow \text{O}^-\cdot\text{O}^- + \text{H}_2\text{O} + e^- \]

where * presents an active site on NiOOH surface, and O*-O*, OO*-OH*, HO*-OH*, O*-OH* indicates intermediates along the OER path.

Reaction free energies ($\Delta G$) for these four elementary steps can be calculated based on the following formula, where $\Delta G_i (i = 1 ~ 4)$ were calculated at $U = 1.23$ V (vs. RHE) and $G_H = 1/2G_{H_2}$ in this work:

\[
\Delta G_1 = \Delta G_{\text{OO}^-\cdot\text{OH}^-} - \Delta G_{\text{O}^-\cdot\text{O}^-} + G_H - G_{\text{H}_2\text{O}} - eU \\
\Delta G_2 = \Delta G_{\text{HO}^-\cdot\text{OH}^-} - \Delta G_{\text{OO}^-\cdot\text{OH}^-} + G_{\text{H}_2\text{O}} - G_{\text{H}} - eU \\
\Delta G_3 = \Delta G_{\text{O}^-\cdot\text{OH}^-} - \Delta G_{\text{HO}^-\cdot\text{OH}^-} + G_H - eU \\
\Delta G_4 = \Delta G_{\text{O}^-\cdot\text{O}^-} - \Delta G_{\text{O}^-\cdot\text{OH}^-} + G_H - eU
\]

The Gibbs free energy ($\Delta G$) for each step can be calculated as:

\[ \Delta G = \Delta E + \Delta ZPE - T\Delta S \]

The thermodynamic overpotential, denoted as $\eta_T$, is a significant symbol used to describe the OER reactivity, referenced with the Reversible Hydrogen Electrode potential (RHE). The thermodynamic overpotential is calculated with the following equation:

\[ \eta_T = \eta_{RHE} - U \]
\[ \eta = -\frac{\Delta G_{\text{max}}}{e} - 1.23 \]

So the higher thermodynamic overpotential means lower OER activity.

**Models**

The crystal structure of \( \beta \)-NiOOH belongs to the \( P_3m_1 \) space group with lattice parameters of \( a = 2.98 \) Å, \( b = 2.98 \) Å, and \( c = 4.58 \) Å. Our selected bulk structure contains uniform \( \text{Ni}^{3+} \) ions, surrounded by six oxygen atoms, forming an octahedral coordination. Each \( \text{Ni}^{3+} \) ion exhibits the electronic configuration \((t_{2g}^6 \epsilon_g^1)\) in a low-spin arrangement.\(^{12}\) Considering the distinctive distribution of O and OH-terminations on different surface along \( z \)-axis, we established the asymmetric facets of NiOOH (001) and NiOOH (00\( \bar{1} \)) in Figure 1. The NiOOH (001) surface is all covered by OH\(^-\) groups, while the NiOOH (00\( \bar{1} \)) surface consists of all O-termination. The interlayer distance of NiOOH (001) was determined to be 1.58 Å, whereas it was 1.51 Å for NiOOH (00\( \bar{1} \)). The Ni-O bond on the surface induces a Jahn-Teller distortion due to the occupation of the \( dz^2 \) orbital, which elongates Ni-O bond along the \( z \)-axis to 2.00 Å with connected to H atom and 1.93 Å at the opposite side without connecting to H atom.

![Figure 1](image-url) The optimized \( \beta \)-NiOOH models of (a) (001) and (b) (00\( \bar{1} \)) surface. (grey color represents Ni atoms, red color represents O atoms, and white color represents H atoms).

**Result and discussion**

*Dual-site OER mechanism on pristine NiOOH (001) and (00\( \bar{1} \))*

It is obviously noticed that a complicated reaction possibly occurs on both (001)
and (00\overline{1}) due to the existence of multi-active surface sites (OH and O), as shown in Fig 1. To evaluate the feasibility of dual-site OER process on both terminations, we explore the catalytic performance of OER based on SSM and UDSM shown in Fig 2a-b, the Gibbs free energy diagram for SSM and UDSM on NiOOH (001) and (00\overline{1}) are in Fig 2c-d. On OH-terminated (001) surface, the potential determining step (PDS) of SSM is O*+OH→OOH* + e− with the thermodynamic overpotential ηT = 1.24 V, while PDS of dual-site mechanism occurs on the step of O-H breakage and O-O formation on O*-O* to form intermediate (OO*-OH*) with thermodynamic overpotential of 0.80 V. The obviously reduced thermodynamic overpotential on UDSM implies OER is more favorably undergo dual-site rather than single-site mechanism.

Figure 2 The reaction pathway of UDSM considered in this work for the (a) β-NiOOH (001) and (b) β-NiOOH (00\overline{1}). The Gibbs free energy diagrams following SSM and UDSM of (c) β-NiOOH

In Fig 2a-b, the Gibbs free energy diagram for SSM and UDSM on NiOOH (001) and (00\overline{1}) are in Fig 2c-d. On OH-terminated (001) surface, the potential determining step (PDS) of SSM is O*+OH→OOH* + e− with the thermodynamic overpotential ηT = 1.24 V, while PDS of dual-site mechanism occurs on the step of O-H breakage and O-O formation on O*-O* to form intermediate (OO*-OH*) with thermodynamic overpotential of 0.80 V. The obviously reduced thermodynamic overpotential on UDSM implies OER is more favorably undergo dual-site rather than single-site mechanism.

![Figure 2 showing the reaction pathway of UDSM considered in this work for the (a) β-NiOOH (001) and (b) β-NiOOH (00\overline{1}). The Gibbs free energy diagrams following SSM and UDSM of (c) β-NiOOH](image-url)
(001) and (d) $\beta$-NiOOH (00$\bar{1}$) under $U = 1.23$ V (vs. RHE). The optimized geometries of involved reaction intermediates during UDSM in (e) $\beta$-NiOOH (001) and (f) $\beta$-NiOOH (00$\bar{1}$).

Similarly, the UDSM for NiOOH (00$\bar{1}$) is also found to be more favorable than SSM, where the PDS also occurs on O-H cleavage in the with only $\eta_1 = 0.77$ V, significantly smaller than 1.62 V in the step of OOH* to desorb O$_2$ and form V$_O$ via SSM pathway. The corresponding four OER intermediates involved in UDSM on (001) and (00$\bar{1}$) are presented in Fig 2e-f, and the intermediate structures of SSM in FigS1-2, respectively. It can be found that the dual-site mechanism is more conducive than SSM (001) or (00$\bar{1}$) surface. This may be due to the UDSM mechanism avoiding the step of adsorption of *OOH intermediates, and the PDS of both surfaces occur at $O^*-O^*+OH^-\rightarrow OO^*-OH^*+e^-$, accompanied by a similar thermodynamic overpotential of about 0.80 V.

**Co/Fe doping effect on dual-site mechanism**

Dual-site based on two different kinds of metals has been found to exhibit enhanced catalytic performance in a cooperative manner.$^{24,25}$ Herein, two kinds of 3$d$-transitional metals (3$d$-TM) (Co and Fe) are doped to create Fe-Ni or Co-Ni heteroatom catalyst to regulate OER performance on $\beta$-NiOOH surface. Since the experiment has shown that the optimal OER performance occurred when the doping ratio of Fe is 25% in NiOOH, we replaced one of the four surficial Ni atoms with Fe or Co (Fe (or Co) : Ni = 1:3) to form Fe-NiOOH and Co-NiOOH in our calculated model, as shown in Fig 3a.$^{26}$ By comparing the structure before and after doping, we found that Fe-doping significantly elongates the bond length of Ni-OH by approximately 0.14 Å (1.98 vs. 2.12 Å) on (001), and Ni-O bond by about 0.07 Å on (00$\bar{1}$), while Co-doping slightly elongates the bond length of Ni-OH or Ni-O by only about 0.02 Å. The formation energy ($E_f$) is calculated to evaluate the structure stability of NiFeOOH and NiCoOOH, based on the expression of $E_f = E_{NiFe(Co)OOH} - E_{NiOOH} - E_{Fe(Co)} + E_{Ni}$. As summarized in Table S1, the calculated $E_f$ values are all negative (-0.43 to -1.93 eV) for (001) or (00$\bar{1}$), indicating structures stabilized by Fe.
The OER reaction pathway of Fe or Co doped \( \beta \)-NiOOH following the UDSM is illustrated in Fig 3b-c. The doping of Co and Fe on the (001) surface raises the thermodynamic overpotential of \( \beta \)-NiOOH (001) by 0.49 V and 0.05 V, respectively. The PDS changes from the O*-O* + OH\(^-\) \rightarrow OO*-OH* + e\(^-\) to the step of OO*-OH* + OH\(^-\) \rightarrow O\(_2\) + OH*-OH* + e\(^-\) (Fig 3b). Enlarged thermodynamic overpotential is also found on (00\(\overline{1}\)) with 0.80 (Co-NiOOH) and 1.16 V (Fe-NiOOH), compared with 0.77 V on the original \( \beta \)-NiOOH (00\(\overline{1}\)), as Fig 3d shows. The PDS of NiOOH (00\(\overline{1}\)) remained on the O-O formation and O-H breakage step of O*-O* + OH\(^-\) \rightarrow OH*-OO* + e\(^-\) (Fig 3c). To make a comparison, reaction pathway following SSM were also explored and shown in Figs S3-4. It can be found that Fe-doping significantly reduces the thermodynamic overpotential to 0.65 and 1.12 V, while Co-doping reduces it to 1.11 and 1.32 V.

To further explore the effect of Fe/Co doping on the UDSM mechanism of the catalyst, we calculated the \( d \)-band center of the active site Ni*. Normally, \( d \)-band of active-metal centers closer to Fermi level corresponds to better OER activity with lower thermodynamic overpotential. According to the \( d \)-band center theory, an upward shift in the \( d \)-band center can reduce the filling of anti-bonding states, thus enhancing the binding strength with oxygen-containing intermediates.\(^{27,28}\) By calculating the \( d \)-band center of Ni atoms at the NiFeOOH (001) and NiCoOOH (001), we found that the doping of Fe shifted the \( d \)-band center of Ni band up to -1.88 eV from the original -2.13 eV, while Co-doping up-shifts to -1.99 eV. The higher energy shift of \( d \)-band leads to stronger adsorption of intermediates onto Ni-site, which leads to the unfavorable subsequent \( O_2 \)-desorption. Therefore, the PDS of OER reaction along the UDSM after Co/Fe doping shifts to OO*-OH* + OH\(^-\) \rightarrow OH*-OH*+O\(_2\) + e\(^-\) on (001), and hence increases the thermodynamic overpotential by 0.49 and 0.05 V. However, for the (00\(\overline{1}\)) surface, the \( d \)-band center of Ni decreased by 0.71 eV after Fe doping, making NiFeOOH (00\(\overline{1}\)) require a higher thermodynamic overpotential for intermediate adsorption under the UDSM. However, no significant change was observed after Co doping (NiOOH: -2.47 eV vs NiCoOOH: -2.34 eV).
Thus, the required thermodynamic overpotential for NiCoOOH does not change significantly.

Figure 3 (a) The optimized geometries of Fe and Co-doped at NiOOH (001) and NiOOH (00\(\bar{T}\)).

The Gibbs free energy diagrams under \(U = 1.23\) V (vs. RHE) for OER under UDSM on the doped (b) NiOOH (001) and (c) NiOOH (00\(\bar{T}\)) surfaces. (d) thermodynamic overpotentials for considered structures with UDSM.

**Dual-site reaction on heterojunction NiOOH@FeOOH and NiOOH@CoOOH**

Previous experiments have found that heterostructure NiOOH/FeOOH and NiOOH/CoOOH have excellent OER performance.\(^{29-31}\) We attempt to use FeOOH or CoOOH as substrates to construct heterostructures of NiOOH@FeOOH and NiOOH@CoOOH, to evaluate the substrate effect on the OER performance under SSM and UDSM. The calculated binding energies \((E_b)\) are all negative (-3.18 to -1.07 eV in Table S2) based on the formula of \(E_b = E_A@B - E_A - E_B\) (A and B refer to NiOOH and FeOOH or CoOOH), which well supports the previous experimentally synthesized heterojunctions of NiOOH@FeOOH and NiOOH@CoOOH. As indicated in Fig 4a, the thermodynamic overpotentials of UDSM for NiOOH@FeOOH (001) and NiOOH@CoOOH (001), are 0.83 V and 0.85 V, similar to 0.80 V of NiOOH (001), with the PDS remained at the step of \(O^*-O^* + OH^- \rightarrow OO^*-OH^* + e^-\).

Conversely, both NiOOH@CoOOH and NiOOH@FeOOH (001) exhibit more
difficult to follow SSM due to larger overpotentials of 2.18 and 1.94 V (Fig S5). This calculated result is well consist with our previous work that the traditional SSM mechanism is unfavorable to occur on NiOOH@FeOOH due to larger overpotential of 2.42 V, while UDSM mechanism significantly reduced the overpotential to only 0.76 V and is closer to the experimentally measured 292 mV at a current density of 500 mA cm\(^{-2}\). Differently, NiOOH@CoOOH (00\(\overline{1}\)) and NiOOH@FeOOH (00\(\overline{1}\)) significantly reduce the thermodynamic overpotentials to 0.76 and 0.49 V under UDSM mechanism in Fig 4c, with the different PDS of O*-O* + OH\(^-\)→OO*-OH* + e\(^-\) and OO*-OH* + OH\(^-\)→HO*-OH* + O\(_2\) + e\(^-\). Meanwhile, the SSM mechanism was also promoted by constructing the heterojunction on (00\(\overline{1}\)) facet, by reducing the thermodynamic overpotentials to 0.97 and 0.93 V for NiOOH@CoOOH and NiOOH@FeOOH, respectively (Fig S6).

To gain a distinct analysis, the \(d\)-band center of active Ni* is analyzed for NiOOH@CoOOH and NiOOH@FeOOH. Loading CoOOH/FeOOH on the \(\beta\)-NiOOH (001) surface results in the Ni* \(d\)-band center of the reaction site moving away from the Fermi level (Fig S7), this results in the need for a larger thermodynamic overpotential for Ni to adsorb the intermediates. However, as Fig 4d shows, the \(d\)-band center of Ni1 and Ni2 for NiOOH@FeOOH (00\(\overline{1}\)) was calculated to be -1.96 and -1.92 eV, indicating an apparent 0.51 and 0.55 eV shift toward Fermi level. This may be due to the lattice strain caused by the elongation of the Ni-O bond resulting from the loading of FeOOH, the length of the Ni-O bond on the surface was extended from 1.92 to 1.99 Å after the combination of FeOOH. As a result, the Ni-site in NiOOH@FeOOH exhibits better OER activity than pure NiOOH, leading to enhanced adsorption on adjacent sites after O-H cleavage, therefore with a change in the PDS. This change in the PDS results in a significant reduction in thermodynamic overpotential. The interfacial electronic distribution of the heteroconjunction is also analyzed, which mainly exhibits physical interaction between interlayer O and OH. The 1\(st\)-layer NiOOH is negatively charged with -0.52 |e| distributed on NiOOH (001). After substituting the supports with CoOOH or FeOOH, the charge of surficial layer
NiOOH are -0.55 and -0.57 |e| for NiOOH@CoOOH and NiOOH@FeOOH by attracting more electrons, respectively. Oppositely, the surface NiOOH layer exhibits smaller positive charge of +0.60 and +0.63 |e| after supported by CoOOH or FeOOH substrates, compared to the original +0.66 |e| of NiOOH on (001) facet, as plotted in Fig. S8.

Figure 4 (a) The calculated potential energy diagrams for OER under UDSM mechanisms on the doped NiOOH@Fe(Co)OOH (001). (b) Structures of O*-O* on NiOOH@Co(Fe)OOH (001) and NiOOH@Co(Fe)OOH (001). (c) The calculated potential energy diagrams for OER under UDSM mechanisms on the doped NiOOH@Fe(Co)OOH (001). (d) The change of d-band center on heterojunction NiOOH@FeOOH (001) and NiOOH@CoOOH (001).

The thermodynamic overpotential of NiOOH along different reaction mechanisms under doping with transition metals and combining with other heterostructures is summarized in Fig 5. NiOOH (001) is the most beneficial to the UDSM mechanism without any regulation, but the thermodynamic overpotential of NiOOH (001) decreases along the UDSM mechanism after loading CoOOH/FeOOH. The NiOOH@FeOOH (001) structure shows a remarkably low thermodynamic overpotential of only 0.49 V. The excellent performance exhibited by NiOOH@FeOOH (001) is attributed to the significant upward shift in the d-band
center of Ni due to the loading of FeOOH, which promotes the adsorption of $\text{OOH}^\ast$ and promotes the PDS thermodynamically. The doping of transition metals causes an upward shift in the $d$-band center of Ni in NiOOH (001), which enhances the adsorption of intermediates at the reaction site. This results in difficulties in subsequent $\text{O}_2$ desorption and an increase in the required thermodynamic overpotential for the reaction. Due to the differences in structural properties between 001 and 00$\bar{1}$, the doping of transition metals Fe and Co results in a decrease in the $d$-band center of Ni in NiOOH (00$\bar{1}$), weakening the adsorption strength of intermediates. It is evident from Fig. 5 that NiOOH (00$\bar{1}$) is more conducive to the reaction of OER under the dual-site UDSM mechanism than NiOOH (001). Through Bader charge analysis, it can be found that the charge distribution on the (001) end face is relatively uniform. The charge difference between adjacent Ni atoms on the surface layer of the (001) plane is 0.08 |e|, whereas the charge difference between adjacent Ni atoms on the (00$\bar{1}$) plane is only 0.01 |e|, which may explain why (00$\bar{1}$) is more conducive to the synergistic effect of dual site.

**Figure 5** Comparison of thermodynamic overpotentials for the oxygen evolution reaction (OER) through the SSM and UDSM under different modulation modes. (a) NiOOH (001) surface. (b) NiOOH (00$\bar{1}$) surface.
**Dual-site mechanism of the compressed NiOOH**

Physical regulation is another common modulating method which involves applying tensile and compressive strains along the horizontal plane to adjust the electronic filling characteristics of the reaction site and regulate the catalytic performance of the catalyst.32–34 Herein, we attempted to compress the NiOOH (001) and NiOOH (00\(\bar{1}\)) surfaces and measure the OER performance of the compressed structures. Compression was applied proportionally to NiOOH (001) and NiOOH (00\(\bar{1}\)) along the x-axis and the y-axis, as **Fig 6a** shows. Compared to NiOOH (001), NiOOH (00\(\bar{1}\)) has a lower compressibility limit ratio. As the compression ratio increases, the Ni-O bond lengths consistently decrease. Specifically, the Ni-O bond length on the NiOOH (001) surface shortens by an average of 0.04 Å after 4% compression. Similarly, the Ni-O bond length on the NiOOH (00\(\bar{1}\)) surface shortens by an average of 0.05 Å after 8% compression (**Table S3**).

**Figure 6** (a) The lengths of Ni-Ni bonds change with compression. (b, c) Variation of thermodynamic overpotential with compression ratio for NiOOH (001) and NiOOH (00\(\bar{1}\)) under the UDSM.

**Figs 6b** and **c** demonstrate the thermodynamic overpotential exhibited by NiOOH under the UDSM mechanism across various compression ratios. It is obvious that compressing the structure on either the (001) surface or the (00\(\bar{1}\)) surface, does not provide any benefits for catalyzing the OER through the UDSM mechanism. As the...
lattice is compressed by 4%, the thermodynamic overpotential of the PDS increases to 1.22 V on the (001) surface, and increases to 1.47 V on the (00$ar{1}$) surface when compressed to 8% (Fig S9-10), higher than that found for the uncompressed NiOOH.

Meanwhile, the PDS of OER reaction still occurs at O*-O* + OH$^-$ → OO*-OH* + e$^-$ on both (001) and (00$ar{1}$) surfaces. However, as Fig S11 shows under the SSM mechanism, compression accelerates the OER reaction rate on the (00$ar{1}$) surface, with the thermodynamic overpotentials of the OER reaction decreases from 1.62 V in the absence of compression to 1.12 V with a compression strain of 8% (Fig S13), the PDS of the (00$ar{1}$) surface transitions from OOH* + OH$^-$ → V_{O} + O_{2} + H_{2}O + e$^-$ to O*+ OH$^-$ → OOH* + e$^-$ after compression.

Previous comparisons of the properties of strained and unstrained materials on Ru (0001) revealed that compressive strain results in a downward shift of the $d$-band center, thereby weakening the interaction. After calculating the $d$-band center of Ni atoms following compression, we found that the $d$-band center of Ni1 and Ni2 atoms on the NiOOH (001) surface decreased by 0.20 eV and 0.19 eV, while the $d$-band center of Ni1 and Ni2 atoms on the NiOOH (00$ar{1}$) surface decreased by 0.59 eV and 0.58 eV, respectively. The decrease in the $d$-band center of the transition metal at the reaction site leads to a weakening of the adsorption of reaction intermediates. Consequently, the free energy change required for the PDS on O*-O* + OH$^-$ → OO*-OH* + e$^-$ of the OER under the UDSM mechanism increases. At the same time, the adsorption of OOH* intermediates by NiOOH under the SSM mechanism also weakens, resulting in an increase in the thermodynamic overpotential for the PDS of O*+ OH$^-$ → OOH* + e$^-$ on the (001) surface under the SSM mechanism, which is 1.42 V with a compression rate of 4% (Fig S12, S13).
Conclusion

By employing DFT calculations, the chemical and physical regulation of OH-terminated NiOOH (001) and O-terminated (00\overline{1}) are carried out to evaluate the effect on OER performance undergoing dual-site and single-site mechanism. The dual-site mechanism (UDSM) was demonstrated to be more favorable on pristine NiOOH (001) and (00\overline{1}), with significantly lower overpotentials of 0.80 and 0.77 V than single-site mechanism (SSM) with 1.24 and 1.62 V, respectively. Chemical Fe- or Co-doping has little effect even increase the overpotential of OER along UDSM on both (001) and (00\overline{1}) facets. By constructing the heterstructures of NiOOH@CoOOH and NiOOH@FeOOH, the overpotentials of UDSM on (001) vary negligible while it on (00\overline{1}) is significantly reduced to 0.49 V (v.s. 0.77 V) after NiOOH supported on FeOOH. The physical compression within 4% on NiOOH (001) and 8% on NiOOH (00\overline{1}) indicates that compression is not conducive to promote OER process undergoing UDSM. The inherent electronic variation of d-band center of the active Ni and interfacial electron distribution between surface and substrates are analyzed to illustrate the OER performance by regulation. The explored UDSM in this work is a favorable and important OER path on the catalyst surface with multi-active sites. LOM mechanism is applicable for the catalyst surface covered with OH- or O- group which participates in the OER process, rather than other terminated groups. The chemical and physical regulation methods will provide a guide for designing the efficient electrocatalysts, although the coupling chemical and physical effects on OER performance are valuable to be further investigated in the future work.

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