Atomic-level insight into super-efficient electrocatalytic oxygen evolution on iron and vanadium co-doped nickel (oxy)hydroxide

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It is of great importance to understand the origin of high oxygen-evolving activity of state-of-the-art multimetal oxides/(oxy)hydroxides at atomic level. Herein we report an evident improvement of oxygen evolution reaction activity via incorporating iron and vanadium into nickel hydroxide lattices. X-ray photoelectron/absorption spectroscopies reveal the synergetic interaction between iron/vanadium dopants and nickel in the host matrix, which subtly modulates local coordination environments and electronic structures of the iron/vanadium/nickel cations. Further, in-situ X-ray absorption spectroscopic analyses manifest contraction of metal-oxygen bond lengths in the activated catalyst, with a short vanadium-oxygen bond distance. Density functional theory calculations indicate that the vanadium site of the iron/vanadium co-doped nickel (oxy)hydroxide gives near-optimal binding energies of oxygen evolution reaction intermediates and has lower overpotential compared with nickel and iron sites. These findings suggest that the doped vanadium with distorted geometric and disturbed electronic structures makes crucial contribution to high activity of the trimetallic catalyst.

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Hydrogen as an energy-dense and carbon-neutral fuel is an ideal alternative to the limited fossil fuels to sustain the fast increase in energy consumption by human society. Water splitting to hydrogen and oxygen \((\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2)\), driven by electric power generated from renewable energy sources, is known as a promising approach to hydrogen production in a large-scale\(^1\). To this end, one of the crucial challenges is to develop inexpensive electrocatalysts that are highly active and durable for water oxidation and proton reduction.

Among the reported non-noble metal catalysts for oxygen evolution reaction (OER), Ni-based bimetal oxides\(^2\)-\(^8\), especially NiFe layered-double-hydroxides (LDHs) (refs.\(^9\)-\(^16\)), have drawn intensive attention due to their excellent OER performance in alkaline media. Much recent research revealed that the incorporation of a third transition metal into NiFe oxides/hydroxides to form NiFeM (M = Co (refs.\(^17\)-\(^19\)), Mn (ref.\(^20\)), Cr (refs.\(^21\),\(^22\)), and Al (refs.\(^23\),\(^24\))) ternary complexes could further enhance the intrinsic OER activity of the Ni–Fe (oxy)hydroxide catalyst in different extents\(^25\). In another aspect, the unary vanadium (oxy)hydroxide was demonstrated to be a highly active OER electrocatalyst in alkaline solution\(^26\). Some very recent studies discovered that incorporation of V into Ni-based oxides/(oxy)hydroxides could effectively enhance the OER activity of the catalysts\(^27\)-\(^30\). However, the questions remain on whether V has substitutionally doped into the lattices of host materials and if so, how V dopant interplays with other metal ions co-existing in a catalyst material, and how the doped V cations contribute to the high OER activity of the host materials. To our knowledge, to date, there is no report on in-depth spectroscopic studies of local coordination environments and electronic structures for the V-containing bi- and trimetal (oxy)hydroxide OER catalysts in both rest and activated states. In very recent years, several groups made in-depth studies on NiFe (refs.\(^10\),\(^14\)-\(^15\),\(^31\)-\(^34\)), FeCo (ref.\(^35\)), NiFeCo (ref.\(^36\)), FeCoW (ref.\(^37\)), and NiFeCoCe (ref.\(^38\)) oxides/(oxy)hydroxides by employing X-ray absorption spectroscopy (XAS), especially operando XAS measured during electrolysis of a catalyst at a preset applied potential. The results obtained from these significant studies provided some crucial information for understanding the origin of high activity of these catalysts and for identifying the authentic active sites in the catalysts.

In light of the reports mentioned above, we prepared a series of Fe/V co-doped, Fe- or V-doped, and pure Ni (oxy)hydroxides as ultrathin nanosheets (NSs) on hydrophilic carbon fiber paper (CFP), and made comparative studies on these OER catalysts by X-ray photoelectron spectroscopy (XPS) and ex-situ/in-situ XAS, combined with density functional theory (DFT) calculations. The Fourier and wavelet transform (FT/WT) analyses of the extended X-ray absorption fine structure (EXAFS) data demonstrate the substitutional occupation sites of Fe and V dopants in Ni(OH)\(_2\) lattices, consistent with the results obtained from theoretical calculations. Moreover, XPS and XAS analyses reveal the synergetic interaction of Fe, V, and Ni cations in the NiFe\(_{0.5}\)V\(_{0.5}\) catalyst, which sublimates modulates local coordination environments and electronic structures of Ni/Fe/V cations in the catalyst. Further in-situ XAS studies manifest a different extent of shrinkage of metal–oxygen bond lengths in the activated catalyst, with a short V–O1 bond distance of 1.65 Å. DFT calculations indicate that the V site of the Fe/V co-doped Ni (oxy)hydroxide gives near-optimal binding energies (BEs) of OER intermediates, and point to the higher OER activity of V site compared to that of Ni and Fe sites.

### Results

**Fabrication and characterization of Ni\(_{1-x}\)Fe\(_x\)\(_{1-x}\)V\(_x\) (oxy)hydroxide catalysts (0 ≤ x ≤ 1), namely NiFe, Ni\(_3\)V, Ni\(_3\)Fe\(_{0.67}\)V\(_{0.33}\), Ni\(_4\)Fe\(_{0.5}\)V\(_{0.5}\), Ni\(_3\)Fe\(_{0.67}\)V\(_{0.33}\), and pure Ni (oxy)hydroxides were directly grown on hydrophilic CFPs by hydrothermal synthesis (Fig. 1 and Supplementary Fig. 1). The atomic ratios of different metals in the as-prepared catalysts were determined by analyses of inductively coupled plasma optical emission spectroscopy (ICP-OES, Supplementary Table 1).

The powder X-ray diffraction (PXRD) patterns (Supplementary Fig. 2) indicate that NiFe\(_1\)–\(_x\)V\(_x\) are isostructural to \(\alpha\)-Ni (OH)\(_2\) (JCPDS Card No. 38-0715). The reflections at 2θ = 11.4° and 22.7°, corresponding to the (003) and (006) lattice planes of NiFe\(_{1-x}\)V\(_x\), slightly shift to larger 2θ values by 0.2° and 0.6°, respectively, relative to those of \(\alpha\)-Ni(OH)\(_2\). The d-spacing values obtained from the (003) and (006) reflections are about 7.65 and 3.81 Å, respectively, with a small contraction compared to those for pure \(\alpha\)-Ni(OH)\(_2\) (d(003) = 7.79 Å and d(006) = 3.91 Å), which is most possibly caused by the substitution of Fe and V atoms for Ni in the lattice sites of the Ni(OH)\(_2\) matrix\(^32\)-\(^39\). Because no extra diffraction peaks are observed in the PXRD pattern, it could be deduced that no separated crystalline phases, such as unary Ni-, Fe-, or V-based oxides/(oxy)hydroxides, are formed during the doping process\(^12\),\(^28\),\(^34\).

Scanning electron microscopic (SEM) images of NiFe\(_{0.67}\)V\(_{0.33}\)/CFP (Fig. 2a) clearly show that the entire surface of each carbon fiber is uniformly coated with the densely interlaced NSs, forming a sharp contrast to the smooth surface of pristine carbon fibers (Supplementary Fig. 3). A close inspection (Fig. 2b) reveals that the interlaced NSs form a porous network structure. Such an open nanoarchitecture built by NiFe\(_{0.5}\)V\(_{0.5}\) ultrathin NSs would afford a mass of electrochemically active sites, an easy penetration of electrolyte, and a good mechanical strength, so as to improve the OER activity and stability of the electrodes\(^4\). The quantitative TEM energy dispersive X-ray spectrum (SEM-EDX) of NiFe\(_{0.5}\)V\(_{0.5}\)/CFP discloses the presence of Ni, Fe, and O elements with a Ni/Fe/V atomic ratio of 74.12:12.83:13.05, which is close to the stoichiometric metal ratio of Ni/Fe/V = 3.0:5.0:5.0. Moreover, the corresponding elemental mappings (Supplementary Fig. 4) illustrate that the Ni, Fe, V, and O elements distribute homogeneously on the surface of carbon fibers.

The bright-field TEM (BF-TEM) image (Fig. 2c) of NiFe\(_{0.5}\)V\(_{0.5}\) NSs illustrates a rippled sheet structure with a dimension around 500 nm, and the lateral TEM image (Fig. 2d) shows the ultrathin NiFe\(_{0.5}\)V\(_{0.5}\) NSs with the thickness of 2.7–4.2 nm. Furthermore, the atomic-resolution BF-TEM image (Fig. 2e) displays clear lattice fringes with an interplanar spacing of 2.67 Å, indexed to the (101) plane of NiFe\(_{0.5}\)V\(_{0.5}\) NSs. The interplanar spacing of lattice fringes is slightly smaller than that of \(\alpha\)-Ni(OH)\(_2\) (2.68 Å) due to the doping of Fe and V for Ni in Ni(OH)\(_2\) lattices. Single atoms, clusters, and small particles of Fe and V species are not observed in aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM) images of NiFe\(_{0.5}\)V\(_{0.5}\) NSs (Supplementary Fig. 5). Meanwhile, both the EDX elemental mappings and linear scanning analysis of the HAADF-STEM image of NiFe\(_{0.5}\)V\(_{0.5}\) NSs with sub-nanometer resolution (Fig. 2f and Supplementary Fig. 6) provide direct-viewing evidence for the uniform distribution of Ni, Fe, V, and O elements in the as-prepared NSs.

In order to clarify the occupation sites of Fe and V dopants in Ni(OH)\(_2\) lattices, we display in Fig. 3 the FT curves of the Fe and V K-edge EXAFS \(k^2\chi(k)\) functions for NiFe\(_3\)Ni\(_2\)V\(_5\), and NiFe\(_3\)V\(_5\). As references, their Ni K-edge FT curves are also plotted (Fig. 3a). The FT curves of the Fe K-edge data of NiFe and NiFe\(_3\)V\(_5\) exhibit two prominent coordination peaks at 1.5 and 2.7 Å that are identical to those of their Ni K-edge data (Fig. 3b), suggesting the substitutional doping of Fe in the Ni (OH)\(_2\) host. Similarly, the FT curves of Ni\(_3\)V and NiFe\(_3\)V\(_5\) each display a prominent V–O peak at 1.4 Å and a V–M (M = Fe, Ni, or V) 4-fold peak at \(\sim 2.05\) Å.
Ni, or V) peak at about 2.8 Å (Fig. 3c), and the high-shell peak of Ni$_3$Fe$_{0.5}$V$_{0.5}$ is weaker than that of Ni$_3$V. The significant decrease in the intensity of the V–M coordination peak in the FT curve of Ni$_3$Fe$_{0.5}$V$_{0.5}$ is most likely caused by the highly distorted local structure of V substituting for the site of Ni. To confirm the substitution of V for Ni in Ni(OH)$_2$ lattices, the WT analysis of the V K-edge data was performed. A maximum at the cross point of $R = 2.8$ Å and $k = 7.8$ Å$^{-1}$ appears in the EXAFS WT map at the V K-edge for Ni$_3$Fe$_{0.5}$V$_{0.5}$ (Supplementary Fig. 7), just like that for Ni$_3$V. This implies the presence of V–Fe/Ni scatterings at...
a distance of around 2.8 Å surrounding V atoms and affords
direct evidence for the substitution of V atoms for the Ni sites in
Ni(OH)₂ lattices. We also made the calculation of the EXAFS
spectra by assuming V adsorption on the Ni-Fe LDH layer or
occupying the interstitial position. It turns out that in both cases
the calculated spectra are quite different from the experimental V
K-edge EXAFS spectra of Ni₁Fe₀.₅V₀.₅ (Supplementary Fig. 8).
Furthermore, DFT calculations suggest that V atoms initially
placed on the top site of surface Ni or O atoms are relaxed to the
interstitial between two LDH layers after structure optimization.
The LDH structure with interstitial doping is noticeably buckled,
with formation energy of ~3.73 eV per V atom, less stable with
regard to LDH with substitutional doping (~5.07 eV per V atom)
(Supplementary Figs. 9, 10), supporting that V atoms occupy Ni
positions in Ni(OH)₂ lattices rather than the interstitial or top
positions of LDH layers. On the other side, from Supplementary
Fig. 11, the nearest-neighbor Pt peak position of V is shifted to the
lower-R side and the second coordination peak to higher-R side
with apparently reduced intensity as compared to that of Fe.
This implies the remarkable different local environment of the
substitutional V from that of Fe in Ni₁Fe₀.₅V₀.₅. The quantitative
parameters extracted from EXAFS curve-fitting (Supplementary
Figs. 12-14 and Supplementary Tables 2-4) further show that the
bond length of V-O (1.72 Å) is significantly contracted with regard
to those of Fe-O (2.00 Å) and Ni-O (2.03 Å).

**Understanding the electronic interaction in Ni₁Fe₁₋ₓVₓ.**
The electronic states of Fe and V in catalysts were investigated by ex-
situ hard X-ray absorption near-edge spectroscopy (XANES).
Generally, in XANES spectra the intensity of the pre-edge peak
depends predominantly on central site symmetry, while the
absorption edge position is correlated to the oxidation state of
central sites. The absorption edges of NiFe, NiV, and
NiFe₀.₅V₀.₅ in the XANES curves of Ni K-edge (Supplementary
Fig. 15a) are all alike to that of the original Ni(OH)₂, indicative of
nearly identical average oxidation states of Ni in the catalysts.
Similarly, the XANES curves of Fe K-edge in Supplementary
Fig. 15b show that the adsorption edges of Fe for NiFe, NiFe₀.₅V₀.₅,
and FeO₂ reference are almost overlapped, manifesting that the average valence states of Fe are close to +3 in the
as-prepared catalysts. Importantly, the V K-edge XANES spectra
of NiV and NiFe₀.₅V₀.₅ exhibit intense pre-edge peaks (Supple-
mentary Fig. 15c), indicating the distorted coordination environment around V atoms in these materials. More interestingly, NiFe₀.₅V₀.₅ shows a higher pre-edge peak than that of
NiV in the V K-edge XANES, implying a higher degree of
octahedral geometry distortion at the V sites in NiFe₀.₅V₀.₅
compared to those in NiV. Additionally, the K-edge absorption positions of NiV and NiFe₀.₅V₀.₅ are more close to those of VO₂
and V₂O₅ than to that of V₂O₃ (inset of Supplementary Fig. 15c),
suggesting that the majority of V ions are in the formal valences
of +4 and +5 in both catalysts.

The as-prepared NiFe₁₋ₓVₓ films were further studied by XPS
and ex-situ soft XAS to gain an insight into the electronic
interaction between Fe/V dopants and Ni atoms at the surface
of catalysts. For NiFe₀.₅V₀.₅ NSs, the Ni 2p spectrum (Fig. 4a)
exhibits two fitting peaks at 872.3 and 854.4 eV along with two
shakup satellites at 878.4 and 860.1 eV, which are characteristic
spin-orbit peaks of Ni²⁺. The Fe 2p region (Fig. 4b), Fe 2p₁/₂ and Fe 2p₃/₂ peaks arise at 724.8 and 711.5 eV, indicative of Fe in the +3 oxidation state (refs. 16,29). The V 2p₃/₂ peak (Fig. 4c) can be deconvoluted into three peaks located at
516.2 eV (V⁵⁺), 515.1 eV (V⁴⁺), and 514.4 eV (V³⁻) (refs. 26,28,29),
demonstrating that the V atoms are predominantly in high oxidation states (+4 and +5) in NiFe₀.₅V₀.₅, together
with a minority of V³⁺, which is consistent with the results
obtained from V K-edge XANES spectra.

It is worthy of note that the Ni 2p BEs for the Fe or V
doped binary and ternary materials are shifted apparently
to higher BEs compared to those of pure Ni (oxy)hydroxide, with
the shift extent in an increasing order of Ni₁Fe₁₋ₓNiV < Ni₁Fe₀.₅V₀.₅ (Fig. 4a, Supplementary Fig. 16a, and Supplementary
Table 5). In contrast, the V 2p peaks for NiV are shifted to lower
BEs relative to the corresponding peaks for VO₂ (ref. 49), and
NiFe₀.₅V₀.₅ displays V 2p₃/₂ peaks at BEs ~0.2 eV lower than
those of NiV (Fig. 4c and Supplementary Fig. 16c). Of particular
interest is that the BEs of Fe 2p₁/₂ and 2p₃/₂ for NiV are lower
than those for FeO₂ (ref. 45), but when half amount of Fe in
Ni₁Fe is replaced by V, NiFe₀.₅V₀.₅ exhibits Fe 2p peaks at BEs
not only considerably higher than those of NiFe but also higher
than FeO₂ (Fig. 4b and Supplementary Fig. 16b), implying that
the Fe dopant acts as an electron accepting site in NiFe but an
electron donating site in an integrated effect when V is co-doped
with Fe into Ni(OH)₂ lattices. These observations suggest the
partial electron transfer from Ni to Fe or V in the binomial (oxy)
hydroxide through strong interfaces (O²⁻) between metal ions,
and from Ni and Fe to O in NiFe₀.₅V₀.₅, which is in good
agreement with the calculated Mulliken charges for V, Fe, and Ni
ions in NiFe₁₋ₓVₓ (Supplementary Table 6).

These speculations are further supported by the Ni, Fe, and V
L-edge XANES spectra shown in Fig. 4d-f. Figure 4d illustrates
that doping Fe or V could intensify the Ni L₁-edge peak (852.5
eV), indicative of partial electron transfer from Ni to the
substituional Fe or V. The intensity of the Fe L₁-edge peak at 709.8 eV for NiFe is also enhanced when V is doped into NiFe
(Fig. 4e). On the contrary, the V L₂,₃-edge peak (518.3 eV) of
NiFe₀.₅V₀.₅ is considerably weakened and shows a red-shift, as
compared with that of NiV (Fig. 4f). The comparative analyses
of XPS and XANES spectra suggest that co-doping of Fe together
with V into Ni(OH)₂ lattices results in more electron transfer to
the V in NiFe₀.₅V₀.₅ compared to that in NiV (Fig. 4c, f and
Supplementary Fig. 16c). The strong interaction among these 3d
metal ions results in synergistic modulation of the electronic
structure of the metal centers of Fe/V co-doped Ni(OH)₂
(refs. 12,22,36,43), and the concerted effect of Ni, Fe, and V metals
with different energy levels of d-band centers could make crucial
contribution to the evident enhancement of OER activity of
hybridized materials. Moreover, we calculated the branching
ratio, L₂/L₁ (L₂ + L₁), at the Fe L₂,₃-edges of NiFe and NiFe₀.₅V₀.₅,
which is approximately 0.74, implying the high-spin of Fe⁴⁺
(ref. 46). And we also calculated the Fe L₂,₃-edge XAS for the
high-spin and low-spin models of Fe⁴⁺ (Supplementary Note 1
and Supplementary Methods). Obviously, the calculated high-
spin L₂,₃-edge XAS could well produce the experimental data
(Supplementary Fig. 17), affording more evidence for the
high-spin configuration of Fe⁴⁺ substituting the Ni sites. Thus,
the valence electronic configurations of Ni²⁺, Fe³⁺, V⁴⁺, and V⁵⁺ are
3d⁸ (t₂g₆e₅), 3d⁵ (t₂g₅e₂g₂), 3d⁴ (t₂g₄e₄), and 3d³ (t₂g₃e₅),
respectively, which are adopted in the following analysis of
valence electron structures of metal ions in NiFe, NiV, and
NiFe₀.₅V₀.₅.

The synergistically electronic interplay of Ni, Fe, and V
cations in NiFe₀.₅V₀.₅ is well explained in light of the analysis of valence
electron structures of metal ions. In term of the result obtained
from DFT calculations that the (Ni₁Fe₀.₅V₀.₅)-OOH models with
some aggregated Fe and V atoms have lower formation energy
and higher OER activity than the models with isolated Fe and V
atoms (vide infra), a Ni-O–Fe–O–V–O–Ni unit (Fig. 4g) is
used to analyze the electronic interaction of Ni, Fe, and V
ions in NiFe₀.₅V₀.₅. For NiFe, the three unpaired electrons in the
π-symmetry (t₂g₈) d-orbitals of Fe³⁺ interplay with the
bridging $O^{2-}$ via $\pi$-donation, while the dominant interaction between the fully occupied $\pi$-symmetry $(t_{2g})$ $d$-orbitals of Ni$^{2+}$ and the bridging $O^{2-}$ is electron–electron repulsion, leading to partial electron transfer from Ni$^{2+}$ to Fe$^{3+}$ (refs. 12,40). The partial electron transfer from $\pi$-symmetry lone pairs of the bridging $O^{2-}$ to $V^{4+}$ and $V^{5+}$ in Ni$_3$V should be stronger than that from the bridging $O^{2-}$ to Fe$^{3+}$ in Ni$_3$Fe, as $V^{4+}$ and $V^{5+}$ have rather low $t_{2g}$ occupancy while Fe$^{3+}$ has a half $t_{2g}$ occupancy. As for the Fe/V co-doped Ni(OH)$_2$, with some of the V and Fe atoms aggregated in the host lattices, when Fe$^{3+}$ accepts partial electrons from Ni$^{2+}$ through the bridging $O^{2-}$ via $\pi$-donation as exemplified by the NiFe (oxy)hydroxide reference, the electron-riched $t_{2g}$ $d$-orbitals of Fe$^{3+}$ could relay electrons to the strongly electron-deficient $t_{2g}$ $d$-orbitals of $V^{4+}$ and $V^{5+}$ through the bridging $O^{2-}$ ions between them, which leads to better delocalization of the $\pi$-symmetry electrons among Ni, Fe, and V in the host matrix. This argument is in good agreement with the XPS and soft XANES results. In Ni$_3$Fe$_{1-x}$V$_x$, the Fe$^{3+}$ and Ni$^{2+}$ with half-full $e_g$ orbitals would have very weak bonding with adsorbed oxygen species, whereas the $V^{4+}$ and $V^{5+}$ with $e_g^0$ orbitals would form too strong bonding with adsorbed oxygen species. To get high OER activity, the bonding strength between transition metal and adsorbed oxygen species should be optimized to fulfill the Sabatier principle47. With increase of the electron density on V by partial electron transfer from Fe and Ni to V through the bridging $O^{2-}$ ions, the high valence states of V could be stabilized under OER conditions, and more importantly, the strong bond strength between V and adsorbed oxygen species could be tuned to a moderate bond strength, which would benefit for releasing O$_2$ from the V site in OER.

**Evaluating the electrochemical OER performance of Ni$_3$Fe$_{1-x}$V$_x$** The electrocatalytic OER performance of Ni$_3$Fe$_{1-x}$V$_x$/CFP were studied in O$_2$-saturated 1 M KOH. The linear sweep voltammograms (LSVs, Fig. 5a) of all as-prepared Ni-based
(oxy)hydroxides show the Ni$^{2+}$/Ni$^{3+}$ oxidation in the potential range of 1.33–1.42 V (all potentials are versus reversible hydrogen electrode (RHE))$^{5,7,43}$.

Figure 5a illustrates that the electrocatalytic activity of Ni$_3$Fe$_{1-x}$V$_x$ depends largely on the co-doping level of Fe and V atoms. Among the as-prepared Fe- or/and V-doped Ni-based binary and ternary catalysts, Ni$_3$Fe$_{0.5}$V$_{0.5}$ exhibits the best OER performance, with low overpotentials of 264 and 291 mV to achieve 100 and 500 mA cm$^{-2}$ current density, respectively (Supplementary Fig. 18). The LSV of Ni$_3$Fe$_{0.5}$V$_{0.5}$, scanning from positive to negative direction to exclude the influence of the Ni$^{2+}$/Ni$^{3+}$ oxidation event on the catalytic current, shows that only 200 mV overpotential is required to attain 10 mA cm$^{-2}$ current density. The OER performance of Ni$_3$Fe$_{0.5}$V$_{0.5}$ is on a par with or even surpasses that of the first-class earth-abundant catalysts reported to date (Supplementary Table 7).

Moreover, the turnover frequency (TOF, based on total amount of metals) of Ni$_3$Fe$_{0.5}$V$_{0.5}$ (0.574 s$^{-1}$) at $\eta = 300$ mV in 1 M KOH is significantly larger than those of Ni$_3$Fe (0.018 s$^{-1}$), Ni$_3$V (0.097 s$^{-1}$), Ni$_3$Fe$_{0.67}$V$_{0.33}$ (0.116 s$^{-1}$), and Ni$_3$Fe$_{0.33}$V$_{0.67}$ (0.195 s$^{-1}$). Figure 5b manifests that the Tafel slope of Ni$_3$Fe$_{0.5}$V$_{0.5}$ (39 mV dec$^{-1}$) is considerably smaller than those of Ni$_3$Fe$_{0.67}$V$_{0.33}$ (59 mV dec$^{-1}$), Ni$_3$Fe$_{0.33}$V$_{0.67}$ (54 mV dec$^{-1}$), Ni$_3$Fe (67 mV dec$^{-1}$), and Ni$_3$V (67 mV dec$^{-1}$). The apparently larger TOF value and smaller Tafel slope of Ni$_3$Fe$_{0.5}$V$_{0.5}$ as compared to those of Ni$_3$Fe and Ni$_3$V indicate that the synergetic effect of co-doped Fe and V plays an important role in facilitating the kinetics of OER and enhancing the intrinsic activity.

The stability of Ni$_3$Fe$_{0.5}$V$_{0.5}$ was assessed by repeated cyclic voltammetry scanning, multi-current step test, and long-term chronopotentiometric experiments. After being subjected to 4000 CV cycles, the OER polarization curve of Ni$_3$Fe$_{0.5}$V$_{0.5}$ almost overlaps with the initial one (Supplementary Fig. 20a), indicating no noticeable loss in catalytic current, and thus, the good accelerated stability of the electrode. Supplementary Fig. 20b shows the $E$–$t$ plot of two cycles of multi-current step curves for Ni$_3$Fe$_{0.5}$V$_{0.5}$ with current density being enhanced from 50 to 500 mA cm$^{-2}$ by five steps. In each step, once a certain current density is set, the potential promptly levels off and maintains constant for 500 s; the multi-current step curve is well repeated in the subsequent cycle. This observation signifies fast mass transportation and good electronic conductivity of the 3D Ni$_3$Fe$_{0.5}$V$_{0.5}$/CFP matrix.$^{13}$ Additionally, the Ni$_3$Fe$_{0.5}$V$_{0.5}$/CFP electrode displays good stability at fixed current densities of 10 and 100 mA cm$^{-2}$, respectively, over 60 h of electrolysis (Fig. 5c), indicating excellent stability of the electrode under testing conditions. The Faradaic efficiency of Ni$_3$Fe$_{0.5}$V$_{0.5}$ evaluated from a chronopotentiometric experiment at a constant current density of 10 mA cm$^{-2}$ for 2 h is close to 100% (Supplementary Fig. 21).

To have a general understanding on the superior activity of Ni$_3$Fe$_{0.5}$V$_{0.5}$, we estimated the roughness factors (RF) and measured the electrochemical impedance spectroscopy (EIS) of all as-prepared Ni-based electrodes. Based on the estimated RF values (Supplementary Fig. 22 and Supplementary Note 2), the OER polarization curves of Ni$_3$Fe$_{0.5}$V$_{0.5}$ were plotted with $J$ normalized by RF values (Supplementary Fig. 23) to estimate the improvement of intrinsic OER activity for the Ni-based (oxy) hydroxides with different Fe and V doping levels.$^{3}$ The specific current density ($J_s = 61.6$ mA cm$^{-2}$) of Ni$_3$Fe$_{0.5}$V$_{0.5}$ at 300 mV overpotential is about 3, 16, and 71 times higher than those of Ni$_3$V, Ni$_3$Fe, and pure Ni (oxy)hydroxides, respectively, which reveals that the co-doping of Fe and V into Ni(OH)$_2$ lattices is much more effective than separately doping Fe or V for improving the specific activity of Ni-based catalysts, and the improved specific activity contributed largely to the high OER performance.
activity of Ni$_2$Fe$_{0.5}$V$_{0.5}$. The Nyquist plots (Fig. 5d) are fitted to a simplified Randles equivalent circuit model (Supplementary Note 3). The very small semicircles in the high frequency zone are attributed to the internal charge-transfer resistances ($R_{\text{ct(int)}}$) of electrodes, and the second semicircles represent the charge-transfer resistances ($R_{\text{ct(1)}}$) at the electrode/electrolyte interface. Both $R_{\text{ct(int)}}$ and $R_{\text{ct(1)}}$ values apparently decreased as Fe and V were co-doped into Ni(OH)$_2$ lattices. The total charge-transfer resistances ($R_{\text{ct}}$) measured at 300 mV overpotential are 4.2, 7.2, 10.0, and 17.2 Ω for the CFP-supported Ni$_2$Fe$_{0.5}$V$_{0.5}$, Ni$_2$V, NiFe, and pure Ni (oxy)hydroxides, respectively (Supplementary Table 9). The excellent charge-transfer capability of Ni$_2$Fe$_{0.5}$V$_{0.5}$ makes a crucial contribution to the superior intrinsic OER activity of the electrode.

**In-situ EC-Raman/XAS studies and theoretical calculations.** To have an in-depth insight into the origin of high activity of the Fe/V co-doped Ni(OH)$_2$, the changes in electronic structures and local atomic environments of Ni$_2$Fe$_{0.5}$V$_{0.5}$ under OER conditions were studied by in-situ electrochemical Raman (EC-Raman) spectroscopy and in-situ XAS. The measurements of in-situ EC-Raman spectra were carried out at the potential range of 1.0–1.8 V in a spectroelectrochemical (PEC) cell filled with 1 M KOH electrolyte (Fig. 6a). When the applied potential was higher than 1.4 V, a pair of well-defined Raman peaks at around 470 and 550 cm$^{-1}$ appeared, which were correlated respectively with the $e_g$ bending and the $A_{3g}$ stretching vibration of Ni–O in the NiOOH-type phase. On the basis of EC-Raman spectra, the host phase of Ni$_{33-\delta}$OOH, formed during the OER process, could provide an electrically conductive, chemically stable, and electrolyte-permeable framework for the Fe and V dopants, which would benefit the electrochemical OER.

Furthermore, the alteration in the local coordination environment of Ni–O/Fe–O/V–O units and the average oxidation states of Ni, Fe, and V centers in Ni$_2$Fe$_{0.5}$V$_{0.5}$ were investigated by in-situ hard XAS (Supplementary Fig. 24). The in-situ Ni K-edge XANES spectra (Fig. 6b) show that the Ni absorption-edge and the white-line are gradually shifted to the higher-energy side as the applied potential is increased from 1.15 to 1.75 V. Accordingly, the Ni–O distance is shortened from 2.04 Å at 1.15 V to 1.90 Å at 1.75 V (Fig. 6c and Supplementary Table 8). The former is close to the Ni–O bond length (2.05 Å) in Ni(OH)$_2$, and the latter is almost identical with the Ni–O bond length (1.88 Å) in NiOOH, which contains a mixture of Ni$^{3+}$ and Ni$^{4+}$ sites. This is in line with the results of in-situ EC-Raman spectroscopy. A similar shift of the Fe white-line peak toward the higher-energy side is also observed with increasing applied potential (Fig. 6d), and the Fe–O distance is shortened slightly from 2.00 Å at 1.15 V to 1.97 Å at 1.75 V (Fig. 6e and Supplementary Table 8), signifying that the oxidation state of Fe is increased from +3 to nearly +4 during the OER electrolysis process of Ni$_2$Fe$_{0.5}$V$_{0.5}$. These FT-XAFS fit results of Ni and Fe K-edges of Ni$_2$Fe$_{0.5}$V$_{0.5}$ in both rest and activated states are consistent with the previous reports. More interestingly, with increasing the applied potential from 1.15 to 1.75 V, the pre-edge peak is slightly decreased in intensity in the in-situ V K-edge XANES spectrum (inset of Fig. 6f), however, it shows identical spectral features to those measured before OER. Similarly, except for the decrease in the intensity of the characteristic peaks, no other obvious change is visible at the ex-situ V L-edge spectra (Supplementary Fig. 25) after OER measurement at 1.75 V. This evidence suggests partial electron transfer to the V 3d orbitals, as their peak intensity is proportional to the unoccupied density of 3d states. Meanwhile, the V–O1 distance is also shortened from 1.70 Å at 1.15 V to 1.65 Å at 1.75 V (Fig. 6g and Supplementary Table 8), which is close to that of the shortest V–O bond length reported for V$^{3+}$ oxides (1.59 Å) while much shorter than that reported for V$^{4+}$ oxides (1.76 Å). The V atoms with such a short V–O bond may have optimal binding capability with oxygen intermediates relative to Ni and Fe atoms, and exhibit enhanced OER activity, as will be illustrated by following theoretical calculations. These in-situ XAS analyses manifest for the first time the contraction of M–M′ and M(M′)–O bond lengths and the short V–O bond distance in the activated V-containing (oxy)hydroxide OER catalysts.

DFT plus Hubbard U (DFT + U) calculations were conducted to have a theoretical understanding on the evident enhancement of OER activity of the Fe/V co-doped Ni(OH)$_2$ from atomic level. It is known that Ni(OH)$_2$ experiences phase transformations during charging and discharging, and its (oxy)hydroxides are proposed to be the active phase for OER. Thus, we...
consider \(\beta\)-NiOOH co-doped by V and Fe atoms with the experimentally optimized doping concentration of Ni:Fe:V = 6:1:1, as well as the systems doped by only V or Fe atom with Ni: V (Fe) = 3:1 (Fig. 7a and Supplementary Fig. 26). The model surfaces are covered by either water molecules or oxygen species that are possibly present in the reaction media. These models with different covered species give very similar results on the catalytic properties (Fig. 7c and Supplementary Table 6).

In the optimized models, the bond lengths between metals and oxygen intermediates are 1.60–1.84, 1.63–1.95, and 1.77–2.05 Å for V, Fe, and Ni, respectively, which are in good agreement with the trend of experimental XAS results. The distinct bond length between O atom and V, Fe, or Ni element is a reflection of their different bond order and bond strength, which is fundamentally governed by the electronic band structure of the material. As revealed by the density of states (DOS) in Fig. 7d, the V, Fe, and Ni atoms in the co-doped Ni(OH)\(_2\) have the \(d\)-band center of 0.09, −2.55, and −2.78 eV, respectively. On the basis of the \(d\)-band theory\(^{54}\), the V atoms with higher \(d\)-band center possess less occupancy of the antibonding states with adsorbed oxygen intermediates, and thus exhibit optimal binding with regard to Ni and Fe atoms (Fig. 7c).

Mulliken charge analysis\(^{55}\) shows partial charges of \(\sim 1.6, 1.0,\) and \(0.8\) e on the V, Fe, and Ni sites, respectively, signifying the stronger metallicity of V atoms and higher chemical activity. Although DFT calculations cannot identify the exact valence for each metal in multi-metal materials, the trend of the partial charges on the V, Fe, and Ni sites obtained from Mulliken charge analysis is consistent with that of the valences of V\(^{4+}\), Fe\(^{3+}\), and Ni\(^{2+}\) estimated on the basis of XANES and XPS. Moreover, the Ni (oxy)hydroxide systems without V doping are half-metal finite DOS solutions at different potentials (\(T = 298\) K). The two-way arrow indicates the overpotential of the rate-limiting step.

**Fig. 7** DFT theoretical models. **a** Side views of the Fe/V co-doped Ni (oxy)hydroxide model for DFT calculations, whose (101) surface is exposed for OER catalysis. **b** Structures and BEs of an OH*, O*, and OOH* intermediates adsorbed on the V site of the model in **a** with the lowest OER overpotential of 0.25 V. The surface metal atoms are covered by O species. **c** Volcano plot of OER overpotential versus BE difference between OH* and O* species for various sites of Ni\(_3\)Fe\(_1\)-\(V_x\) (oxy)hydroxide models. For each type of reaction site, various structural models are considered, whose detailed information is given in Supplementary Fig. 28 and Supplementary Table 6. The dashed line is a guide for eyes. **d** Left panel: DOS of the model in **a** and the projected DOS on \(s, p,\) and \(d\) orbitals. Right panel: projected DOS on the \(3d\) orbitals of Ni, Fe, and V atoms in the model. The dashed lines represent the \(d\)-band center for each element. The Fermi level is shifted to zero. **e** Calculated free-energy diagram of OER on the most active site of Ni\(_3\)Fe\(_2\)-\(V_{0.5}\) (oxy)hydroxide in pH 14 solutions at different potentials (\(T = 298\) K). The two-way arrow indicates the overpotential of the rate-limiting step.
In the previously reported mechanism for 3d metal-based (oxy) hydroxide catalysts in alkaline media, the OER undergoes through following four elementary steps:

\[ \text{OH}^- + \text{OH}^- \rightarrow \text{O}^+ + \text{H}_2\text{O(l)} + e^- \]  

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

\[ \text{OOH}^+ + \text{OH}^- \rightarrow * + \text{O}_2(g) + \text{H}_2\text{O(l)} + e^- \]

where * represents an active site on the catalyst surface; OH*, O*, and OOH* are the oxygen intermediates. To evaluate the OER activity of the Fe and/or V doped or pure Ni (oxy)hydroxide systems, we computed the BEs of oxygen intermediates on various metal sites. The Gibbs free energy for each reaction step and theoretical OER overpotentials were calculated with the standard hydrogenc electrode (SHE) method.

As displayed in Fig. 7c, the OER overpotentials of doped Ni (oxy)hydroxides follow a volcano-shape relation with the BE difference between OH* and O* (or OOH*) species. In particular, oxygen binding on the Fe and Ni sites is relatively weak, i.e., \( E_{\text{OER}} = 1.15 \text{ eV} \) and \( E_{\text{OER}} = 2.24 \text{ eV} \). As a consequence, formation of OH* and O* species encounters large potential barriers (Supplementary Fig. 2a, b) and will limit the reaction rate of OER process. Large overpotentials of 0.72--0.79 and 0.84--1.08 V are obtained for the Fe and Ni sites, respectively, indicating their low activity for OER. By contrast, the V sites provide much stronger but moderate oxygen binding strength, i.e., \( E_{\text{OER}} = 0.47--0.79 \text{ eV} \) and \( E_{\text{OER}} = 1.61--2.23 \text{ eV} \) and give near-optimal BEs of OER intermediates. Reactions to the formation of OH* and O* species are readily accessible, while formation of OOH* experiences the largest potential barrier and limits the OER rate, giving overpotentials of 0.25--0.63 V, which are much lower than those for Ni and Fe sites. Therefore, the highest activity is predicted on the V site of the co-doped Ni (oxy) hydroxide with some of the V and Fe atoms aggregated (Fig. 7b). Such V sites provide strong OOH* binding relative to O* species, and the overpotential is even lower than that of the Fe-based catalyst RuO\(_2\), i.e., 0.40 V for the (110) surface according to our calculations. The origin of overpotentials is clearly revealed by the free-energy diagrams as shown in Fig. 7e and Supplementary Fig. 29. The largest potential step at the equilibrium potential \( (U = 0.402 \text{ V}) \) indicates the rate-limiting step (RLS) and corresponding overpotential, by overcoming which all the OER steps become downhill and thus can occur spontaneously from the thermo-dynamic point of view (Supplementary Note 4). In general, the theoretical OER overpotentials follow the same trend as the experimental values: Fe/V co-doped < V-doped < Fe-doped < undoped Ni (oxy)hydroxide (Supplementary Fig. 28 and Supplementary Table 6). DFT calculations show that the OER activity of V sites doped in Ni\(_2\)Fe\(_{0.5}\)V\(_{0.5}\) was greatly enhanced by the surrounding Ni/Fe next-nearest neighbors, and more importantly, the (Ni\(_2\)Fe\(_{0.5}\)V\(_{0.5}\))-OOH models with some of Fe and V atoms aggregated in NiOOH lattices have lower formation energy and higher OER activity than the models with isolated Fe and V atoms. This inference is agree with the statement made by Bell and Calle-Vallejo et al. that for Fe-doped Ni (oxy)hydroxides the surrounding Ni neighbors increase the activity of Fe sites.

**Discussion**

In summary, comparative studies on a series of binary and ternary OER catalysts of Ni\(_x\)Fe\(_{1-x}\)V\(_{2}\) (0 ≤ x ≤ 1) demonstrate that synergistically modulating electronic structure of Ni(OH\(_2\)) by co-doping of Fe and V with optimal doping levels could boost the OER activity of Ni (oxy)hydroxides in alkaline solutions. Notably, Ni\(_2\)Fe\(_{0.5}\)V\(_{0.5}\) features an apparently smaller charge transfer resistance and displays considerably higher specific activity compared to Ni\(_2\)V and Ni\(_2\)Fe, which implies a concerted effect of Fe and V on the OER performance of Ni-based (oxy)hydroxides. The FT and WT analyses of EXAFS data attest the substitution of Fe and V atoms for the Ni sites in Ni(OH\(_2\)) lattices, which is supported by the results obtained from theoretical calculations. The comparative studies of Fe/V co-doped, Fe- or V-doped, and pure Ni (oxy)hydroxides by XPS and soft XAS reveal the synergistic interaction among Fe, V, and Ni cations, rooted from quite different valence electronic configurations of these 3d metals. Such interaction subtly influences the electronic structures and local coordination environments of the metals in the ternary catalyst. Accordingly, the XAS results unveil the highly distorted local coordination structure of V and short V-O bond length in Ni\(_2\)Fe\(_{0.5}\)V\(_{0.5}\), which is further shortened under OER conditions.

**Methods**

**Hydrophilic pretreatment of CFP**. Both sides of the cut-out CFP (thickness of 0.18 mm) were first activated by oxygen plasma treatment with RF frequency of 40 kHz for 5 min (Diener Electronic Plasma-Surface-Technology, Germany), to make the CFP substrate have good hydrophilicity. Subsequently, the pretreated CFP was cleaned by sonication in concentrated nitric acid, deionized water, isopropanol, and acetone for 20 min, respectively, and then kept at 45 °C in a vacuum drier for 5 h.

**Fabrication of Ni\(_2\)Fe\(_{0.5}\)V\(_{0.5}\) NS arrays on CFP**. Fe/V co-doped Ni (oxy)hydroxide NS array on CFP was prepared by a hydrothermal method. In a typical fabrication process of Ni\(_2\)Fe\(_{0.5}\)V\(_{0.5}\)/CFP, the solution of NiCl\(_2\)·6H\(_2\)O (0.6 mmol, 142.62 mg), FeCl\(_3\)·6H\(_2\)O (0.1 mmol, 27.03 mg), and VCl\(_3\) (0.1 mmol, 15.73 mg) in deionized water (40 mL) was magnetically stirred for 10 min to form a homogenous solution, to which urea (4 mmol, 240.24 mg) was added with subsequent stirring for 10 min. Afterwards, the prepared solution was transferred to a 50 mL stainless-steel Teflon-lined autoclave and a piece of the pretreated hydrophilic CFP (3 x 4 cm) was placed upright in the middle of autoclave. Next, the autoclave was sealed and heated in an electric oven at 120 °C for 12 h. After cooling the system to room temperature naturally, the resulting CFP with Ni\(_2\)Fe\(_{0.5}\)V\(_{0.5}\) (oxy)hydroxide NS array was washed with deionized water and ethanol by the assistance of ultrasonication for three times to remove the loosely attached materials, and then dried in vacuum oven at 50 °C overnight. A series of reference electrodes, Ni(OH)\(_2\), NiFe, Ni\(_2\)V, Ni\(_2\)Fe\(_{0.3}\)V\(_{0.7}\), and Ni\(_2\)Fe\(_{0.5}\)V\(_{0.5}\) (oxy)hydroxide NS arrays on CFP, were prepared by the essentially identical procedure. The doping level of Fe and V atoms in the host structure of Ni(OH)\(_2\) was controlled by precisely regulating the molar ratio of Ni/Fe/V salts in the precursor solution, while with the same total amount of metal ions in the initial solutions (Ni\(_2\)Fe\(_{0.3}\)V\(_{0.3}\) = 0.8 mmol). For
each hydroxide catalyst, at least three electrodes were prepared and used for the spectroscopic and catalytic measurements.

**Physical and chemical characterizations.** SEM images, EDX, and elemental mappings were measured on a Hitachi SU8220 cold field-emission scanning electron microscope operated at an acceleration voltage of 5 and 15 kV, respectively. BF-TEM and HRTEM were collected on a FEI Tecnai G2 F30 S-TWIN transmission electron microscope with an acceleration voltage of 300 kV. Aberration-corrected HAADF-STEM images, EDX elemental mappings and linear scanning analysis were collected on JEOL ARM200F microscope with STEM aberration corrector operated at 200 kV. XP spectra were taken on a ThermoFisher ESCALAB™ 250Xi surface analysis system using a monochromatized Al Ka small-spot source, and the corresponding BEs were calibrated by referencing the C 1s to 284.8 eV. PXRD patterns were obtained with a Rigaku SmartLab 90 using Cu Ka radiation (λ = 1.54056 Å), and the layers were collected in Bragg-Bretanimo mode in the 2θ range from 10° to 70° at a scan rate of 5° min⁻¹. The loading amounts and elemental compositions of catalysts were determined by ICP-OES on an Optima 2000 DV spectrometer (Perkin-Elmer). The as-prepared b- or trimetallic (oxy)hydroxide array on CFP was immersed in aqueous NaOH (1 M KOH) solution, rinsed in distilled water, and the solution was evaporated to dry by deionized water and sonicated for 15 min. All reported ICP-OES results were the average values of at least three independent experiments.

**In-situ EC-Raman measurements.** In-situ EC-Raman spectra were recorded with an XploRA confocal microscope Raman system. A 50× magnification long working distance objective was used. The laser excitation wavelength of 785 nm was generated using a He-Ne laser (1 mW). The Raman spectra shown in the experiment were collected during 30 s for one single spectrum curve one time, accumulation four times. A custom-made PEC cell with a GCE covered with Ni1Fe1-V0.5 (oxy)hydroxide catalyst film, a platinum mesh counter-electrode, and a saturated calomel reference electrode (SCE, 0.242 V versus SHE) was used for EC-Raman measurements. The electrolyte solution (1 M KOH) was saturated with Ar gas before injected into the cell.

**Ex-situ soft and hard XAS measurements.** The soft XAS of Ni L2,3-edge, Fe L2,3-edge, and V L2,3-edge were measured on beamline BL12 at the National Synchrotron Radiation Laboratory (NSRL, China) in the total electron yield (TREY) mode by collecting the sample drain current under a vacuum better than 1 × 10⁻⁷ Pa. The beam from the bending magnet was monochromatized by utilizing a varied line-spacing plane grating and refocused by a toroidal mirror. The energy range is 100–1000 eV with an energy resolution of ~0.2 eV. To optimize the XAS measurements, we collected several XAS spectra at different positions on each sample. No big difference was found among these XAS spectra due to the uniformity of the sample. For annotating the effect of different sample concentration and measurement conditions on the intensity of characteristic XAS peaks, the data at Ni, Fe, and V L-edge were normalized following the method proposed in literature⁶⁵. The Ni, Fe, and V K-edge XANES and EXAFS spectra were measured on beamline BL14W1 at Anhui Synchrotron Radiation Facility (SSRF, China) with a ring electron current of 250 mA at 3.5 GeV. The Ni, Fe, and V K-edge XAS spectra of NiFe1-V0.5 (oxy)hydroxide materials were performed in the fluorescence mode using a Lytle detector, while the reference samples (V2O5, V2O3, Fe2O3, and Fe3O4) with appropriate absorption edge jump were measured in transmission mode. The conventional fluorescence detection measurements, the background from elastic and Compton scattering was reduced using a combination of Z-1 filters (three absorption lengths of Ti (Mn, Co) for V (Fe, Ni) K-edge spectra) with Soller slits.

**In-situ XAS measurements.** The in-situ XANES and EXAFS data were obtained on beamline BL14W1 at SSRF in the fluorescence mode using a Lytle detector with a step-size of 0.25 eV at room temperature. For the in-situ XAS measurements, an electrochemical workstation (CHI 660E) and a custom-made PEC cell were used. The PEC cell was equipped with a copper frame induced working electrode, a platinum plate counter electrode, and a Hg/HgO (1 M KOH) reference electrode in 1 M KOH solution (Supplementary Fig. 24). For installation of in-situ XAS setup, the side of Kapton film was faced to the fluorosce mode. The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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**Electrochemical measurements.** All electrochemical measurements were carried out at 25 °C on a CHI 660E potentiostat. A three-electrode H-shaped cell was used with the as-prepared Ni-based (oxy)hydroxide/CFP (0.2 cm²) as the working electrode, a platinum mesh (Tjaida) as the counter electrode, and a Hg/HgO (1 M KOH, Tjaida) as the reference electrode. Prior to each electrochemical experiment, the cell was washed and stored in 0.5 M H₂SO₄, the counter electrode was cleaned in aqua regia for 30 s to remove any oxidative and deposited species during OER process; the electrolyte (1 M KOH) was degassed by bubbling oxygen for 30 min; the reference electrode was corrected against another unused Hg/HgO electrode stored in 1 M KOH solution. The measured potentials versus Hg/HgO were converted to the potentials versus RHE by the following equation:

\[
E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 pH + 0.1977 \text{V} + 0.0989 \text{V} \quad \text{(SHE)}
\]

(5)

Five cycles of CV were executed at a scan rate of 50 mVs⁻¹ prior to the measurement of OER polarization curves at 5 mVs⁻¹, and the Tafel slopes were derived from the corresponding OER polarization curves. For all polarization curves presented in the paper, the iR values were manually corrected with the series resistance (Rₛ) on the basis of the equation:

\[
E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 pH + 0.1977 \text{V} + 0.0989 \text{V} - iR_s \quad \text{(SHE)}
\]

(6)

The compensated ohmic, Rₛ values were obtained from the fittings of electrochemical impedance spectra.

**Computational method.** Spin-polarized DFT calculations were performed by the Vienna ab initio simulation package (VASP), using the plane-wave basis with energy cutoff of 500 eV (ref. 64), the projector augmented wave (PAW) potentials⁶⁴, and the PBE functional for the exchange-correlation energy⁶⁴. Grimme’s semi-empirical DFT-D3 scheme of dispersion correction was adopted to describe the van der Waals (vdW) interactions in layered materials⁶⁶. The Hubbard-U correction was applied for better description of the localized d-electrons of Ni, Fe, and V in their (oxy)hydroxides⁶⁷. We chose an effective U-J value of 3.0 eV for V and Fe and 5.5 eV for Ni atoms, close to the literature values⁶⁸,⁶⁹. Mulliken charge analysis⁸⁵ was performed by using SIESTA code⁹⁶ using the plane-wave basis with an energy cutoff of 1000 eV and norm-conserving pseudopotentials.

**Data availability** The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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In this paper, we explore the valence- and element-dependent water oxidation behaviors of NiFeV ternary layer hydroxide nanosheets, and their implications for catalytic water oxidation.

A key finding is the identification of a NiFeV ternary layer hydroxide nanosheet that exhibits high catalytic efficiency in water oxidation. This material is particularly promising for the development of new, efficient catalysts for this critical process.

The results suggest that the catalytic activity can be tuned by adjusting the valence and element composition of the nanosheets, offering new opportunities for the design of advanced catalysts. These findings contribute to the broader understanding of water oxidation mechanisms and the potential for developing sustainable energy solutions.
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Author contributions
J.J. conceived the project, performed most of the experimental work, and drafted part of the manuscript. M.W. conceived and supervised the project, wrote the main part of the paper, and revised the entire paper. J.J., F.S., H.Z., Z.J., W.H., and W.Y. conducted the XAS experiments and analyzed the data. W.Y. wrote the part on XAS results. S.Z. and J.Z. performed the DFT calculations, and S.Z. wrote the part on DFT calculations. J.D. and J.L. made the EC-Raman experiments.

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