Single atom tungsten doped ultrathin α-Ni(OH)₂ for enhanced electrocatalytic water oxidation

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Electrocatalytic water oxidation is a rate-determining step in the water splitting reaction. Here, we report one single atom W⁶⁺ doped Ni(OH)₂ nanosheet sample (w-Ni(OH)₂) with an outstanding oxygen evolution reaction (OER) performance that is, in a 1 M KOH medium, an overpotential of 237 mV is obtained reaching a current density of 10 mA/cm². Moreover, at high current density of 80 mA/cm², the overpotential value is 267 mV. The corresponding Tafel slope is measured to be 33 mV/dec. The d⁰ W⁶⁺ atom with a low spin-state has more outermost vacant orbitals, resulting in more water and OH⁻ groups being adsorbed on the exposed W sites of the Ni(OH)₂ nanosheet. Density functional theory (DFT) calculations confirm that the O radical and O-O coupling are both generated at the same site of W⁶⁺. This work demonstrates that W⁶⁺ doping can promote the electrocatalytic water oxidation activity of Ni(OH)₂ with the highest performance.

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Electrocatalytic water splitting for hydrogen and oxygen generation provides an attractive path to obtain clean energy via the conversion and storage of intermittent solar and wind energies; however, the half reaction of oxygen evolution remains the bottleneck for such progress. The oxygen evolution reaction (OER) is kinetically sluggish and needs the necessary two steps of O–H bond breaking and attendant O–O bond formation, which includes the transfer of four electrons. The design of a considerable OER electrocatalyst is needed. In this case, the noble metal-based catalysts, for example IrO$_2$ and RuO$_2$, exhibit attractive OER activity, but their rare nature hinders their large-scale application. A great many non-noble metal-based alternative catalysts using abundant 3d metals (Fe, Co, Mn, and Ni) have been studied with increasing activity and stability in recent years. In particular, Ni(OH)$_2$-based samples have garnered a great interest with studies showing their encouraging water oxidation potential. In addition, the doping of elemental Fe with Ni(OH)$_2$ at low content levels has been shown to greatly increase the OER performance. However, substantial progress in the development of Ni(OH)$_2$-based catalysts with enhanced activity is still needed.

For the Fe-doped Ni(OH)$_2$ sample, the detailed OER pathways have been shown through several manners of occurrence. In the preliminary works, Fe doping is considered to improve the electrical conductivity and change the electronic structure, anodically shifting the Ni redox potential. Boettcher confirmed that Fe exerted a partial-charge transfer activation effect and then promoted the OER of the Ni sample. By using operando X-ray absorption spectroscopy and computational methods, Bell et al. proposed that the Fe doping in NiOOH produced short Fe–O bonds. These active bond sites were said to have resulted in the high OER performance with low over-potentials and optimal adsorption energies of OER intermediates being observed. Stahl et al. first detected the formation of Fe$^{4+}$ during the OER process by Mössbauer Spectroscopy and reported that the species was not kinetically competent to serve as the active site in water oxidation. Strasser concluded that Fe could suppress the oxidation process of Ni species from $+2$ to $+3$ and help the lower-valent states of the Ni centers have a higher OER activity. The Fe sites in Ni-based hydroxides are almost accepted to be the critical component of the record activity of water oxidation. To further confirm that reactive Fe sites were responsible for the exceptional OER, the introduction of Fe into the Ni$_2$O$_4$H$_4$ from solution was performed with the unaltered conclusion that its precise role remains unclear. Although the replacement of Fe$^{3+}$ to Ni$^{2+}$ in the Ni(OH)$_2$ sample has been shown to enhance oxygen evolution through extensive study, the core part of the water oxidation on the surface of the Ni(OH)$_2$-based sample, that is, the reaction behavior on the exposed/contacted Ni(OH)$_2$ surface is rarely studied and reported. Moreover, the OER performance of Ni(OH)$_2$-based electrocatalysts still needs improvement by doping, and the finding of a suitable element remains to be developed.

On the electrocatalytic process, there is an electric double layer (Helmholtz layer, HL) at the catalyst/solution interface as shown in Supplementary Fig. 1. The electrical circuit is completed through three resistance measures i.e., the catalyst, catalyst/solution interface, and the solution. The HL is important and determining for the final electrocatalytic efficiency owing to the induced capacitive and resistive characteristics resultant from the changing of a solid to solution. In the case of water splitting, the adsorption and desorption behaviors of H$_2$O molecules and OH$^-$ groups in the HL will directly influence the hydrogen or oxygen generation. Therefore, the specifics of the coordination of the exposed elements (such as Ni or Fe) should be studied further to potentially improve the performance. The appropriate chemical environment, the strength of the bond between the electrode and intermediates and the electron migration resistance are the key factors in leading to a significant OER enhancement. Recently, Shin et al. found that both Ni$^{4+}$ and Fe$^{4+}$ played essential roles in the OER. The high spin d$^4$ Fe$^{4+}$ site was favorable for stable O$^-$ radical formation with the low spin Ni$^{4+}$ more favorable for O–O bond coupling. In addition, Zhang et al. reported that the W doping can provide the near-optimal adsorption energies for OER intermediates in FeCo oxy-hydroxide samples, and single-atom doping has been reported to be useful for assisting suitable sites for intermediates formation. It is still then necessary to find one suitable reaction site for achieving both the formation and migration of intermediates.

Herein, we report that W$^{6+}$ doping can boost the OER performance of Ni(OH)$_2$ greatly. Owing to the d$^8$ characteristic, the W$^{6+}$-doping sites exhibit exothermic H$_2$O adsorption and O radical formation reactions, differing from the endothermic reactions otherwise reported. Furthermore, the formation of the O radical and O–O coupling both happen at the W$^{6+}$ sites. In conjunction, the W-doped sample exhibits low reaction potentials at high current densities.

**Results**

**Insight into the water oxidation on Ni(OH)$_2$.** At first, the electrocatalytic processes of Ni(OH)$_2$ were studied to check the interfacial effect on the OER. On the electrocatalytic water oxidation by Ni(OH)$_2$, one obvious process attributable to the Ni$^{2+} \rightarrow$ Ni$^{3+}+e^-$ peak (ca. 1.45 V in Fig. 1a) in the cyclic voltammetry plots was detected. This process happened together with the formation of the O*, which is an essential intermediate (which couples with one OH$^-$ group to generate *OH) for oxygen evolution. Figure 1a gives the CV curve of Ni(OH)$_2$, and the inset shows the corresponding oxygen evolution intermediate pathways: at the low potential (region ➀), *OH generation; in the mid potential (region ➁), the above-mentioned process occurs; and then the O$_2$ will generate under high potential (region ➂). The three simplified processes of water oxidation involve the HL and include *OH species adsorption, *O radical formation, and *OOH transformation and desorption. To detect the interfacial resistance of the corresponding process, three potentials of 1.2, 1.45, and 1.6 V were applied for the electrochemical impedance spectroscopy (EIS) measurement as shown in Fig. 1b. Supplementary Table 1 shows the fitted values based on the equivalent electric circuit (Fig. 1c). Clearly, $R_\text{ct}$, the resistance of the solution and electrode, presented a slightly increasing trend from 10.8 to 17.5 $\Omega$cm$^2$ under the potential of 1.2 to 1.6 V; meanwhile, the $R_{\text{ct}}$, the charge transfer resistance, gave a decreasing trend from 277.4 to 168.6 $\Omega$cm$^2$. The above increasing and decreasing trends suggested the change (Ni$^{2+} \rightarrow$ Ni$^{3+}+e^-$) of the electrode surface. To obtain further information, the change rate of fitted resistance values were carried out as shown in Fig. 1d. The increasing and decreasing rates of 1.45 V compared with 1.2 V are 0.55 and 0.14, respectively, meanwhile, the rates for the 1.6 V condition compared with 1.45 V are 0.05 and 0.29, respectively. The slight change confirms that the process of Ni$^{2+} \rightarrow$ Ni$^{3+}+e^-$ at the lower potential is the decisive step for the overall water oxidation. Based on the above experimental results and analysis, an excellent OER Ni(OH)$_2$-based catalyst should have the suitable outermost orbits for *OH species adsorption and for stabilization of the *O radical. Moreover, if it has the preferred O–O coupling ability, then high water oxidation efficiency will be expected.

Synthesis of W single-atom doped Ni(OH)$_2$. Bare Ni(OH)$_2$ and doped samples were synthesized through the alcoholothermal method using an NiCl$_2$–ethanol and WCl$_6$–ethanol solution...
Ni(OH)₂ under the three potentials of 1.2, 1.45, and 1.6 V. The K₂O solution. Note that the proposed reaction pathways in (Experimental section and Supplementary Fig. 2). Figure 2a shows the XRD patterns of the obtained samples. For bare Ni(OH)₂, (Ni(OH)₂-r), all peaks were assigned to the α-Ni(OH)₂ phase (PDF: 38-0715). The tungsten-doped sample (w-Ni(OH)₂-e) also gave the typical α-Ni(OH)₂ XRD signals with the obvious difference: the peaks of (101) and (110) loaded at 2 theta of 33.4 and 59.9 degree maintained their location, but the peaks of (003) and (006) showed a left shift compared with the Ni(OH)₂-r sample. As we know, for the layered Ni(OH)₂ sample, the shift of the (003) peak to the low diffraction angle suggested that the interlayer spacing between the signal from the octahedral Ni(OH)₆ layer had been broadened. The W element has a more unoccupied outermost electron orbital than Ni, and the replacement of one Ni by one W in the layered Ni(OH)₂ structure was expected to generate some additional adsorption sites on W. In our present work, the ethanol or other relative groups would adsorb on the exposed W sites and then widen the layered structure. When the w-Ni(OH)₂-e sample was treated by ultrasound for 1 min, the typical XRD signals of WO₃, 1%, 2% and 3% WO₃ loaded Ni(OH)₂ samples were tested as shown in Supplementary Fig. 6. Obviously, the WO₃-loaded Ni(OH)₂ samples show the red-shift optical absorption even at a low content (1%), suggesting that W doping of the w-Ni(OH)₂ sample was indeed lattice doping via single- or multi-atomic doping. The X-ray absorption spectroscopy (XAS) measurements were carried out to further confirm the atomic doping of W element. WO₃ and W powder were used as the reference samples. As shown in Fig. 2c, the normalized X-ray absorption near-edge structure (XANES) spectra of W K-edge, the intensity of prominent peak of w-Ni(OH)₂ or WO₃ is higher than W powder, suggesting the oxidized electronic structure of W element in w-Ni(OH)₂. Moreover, the position of the prominent peak of w-Ni(OH)₂ was close to that of WO₃ (10208.07 eV), revealing the dominance of W⁶⁺ in w-Ni(OH)₂. The above observation coincides well with the XPS results. No obvious difference can be detected.

Figure 2b shows the typical UV–Vis absorption spectrum. No obvious main peak shifts or WO₃-based signals could be detected, confirming that the W doping did not change the electronic structure of the Ni(OH)₂ sample. Moreover, the above UV–Vis spectra results suggested the low W content doping or lattice doping, which was thought to have occurred. To further confirm this, the UV–Vis signals of WO₃, 1%, 2% and 3% WO₃ loaded Ni(OH)₂ samples were tested as shown in Supplementary Fig. 6. Obviously, the WO₃-loaded Ni(OH)₂ samples show the red-shift optical absorption even at a low content (1%), suggesting that W doping of the w-Ni(OH)₂ sample was indeed lattice doping via single- or multi-atomic doping. The X-ray absorption spectroscopy (XAS) measurements were carried out to further confirm the atomic doping of W element. WO₃ and W powder were used as the reference samples. As shown in Fig. 2c, the normalized X-ray absorption near-edge structure (XANES) spectra of W K-edge, the intensity of prominent peak of w-Ni(OH)₂ or WO₃ is higher than W powder, suggesting the oxidized electronic structure of W element in w-Ni(OH)₂. Moreover, the position of the prominent peak of w-Ni(OH)₂ was close to that of WO₃ (10208.07 eV), revealing the dominance of W⁶⁺ in w-Ni(OH)₂. The above observation coincides well with the XPS results. No obvious difference can be detected.

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Å, which can be assigned to W–O coordination. Importantly, in comparison with WO₃ (1.31 Å), some appreciable shift of W–O peak (1.39 Å) for w-Ni(OH)₂ can be detected, confirming the different W–O environment. Supplementary Fig. 7 shows the corresponding atomic force microscope (AFM) images of the studied samples, in which Ni(OH)₂-r, w-Ni(OH)₂-e, and w-Ni(OH)₂ show the thickness of 8, 12, and 8 nm, respectively.

Figure 3 gives the electron microscope analysis of the w-Ni(OH)₂ sample. According to the SEM image (Fig. 3a), the layered structure of w-Ni(OH)₂ was found to be clearly evident. The reference samples i.e., Ni(OH)₂-r and w-Ni(OH)₂-e also gave the typical layered image (Supplementary Fig. 8). Figure 3b shows the corresponding TEM result of the w-Ni(OH)₂ sample, the thin layered structure was here further confirmed. The inset shows the typical electronic diffraction spots with the hexagonal structure of α-Ni(OH)₂ clearly present. The TEM images of reference samples can be found in Supplementary Fig. 9, Fig. 3c gives the HADDF image and the corresponding element mapping. Clearly, the Ni(OH)₂ structure was doped by the W element uniformly. To directly find the W in the Ni(OH)₂ lattice, HAADF-STEM was further carried out. As shown in Fig. 3d, the light spots originated from the W element, which had been doped into the lattice and did not change the elements hexahedral arrangement (Fig. 3e).

Supplementary Fig. 10a shows the local enlarged HADDF–STEM image and the corresponding mode of the signal by the W-doped Ni(OH)₂ hexagonal structural unit, clearly suggesting that the signal by W doping has been obtained based on our present synthesized process. Moreover, according to the model of the atomically doped W atoms in the Ni(OH)₂ structure in Supplementary Fig. 10b, the above XAS results confirm the atomic doping of W atoms into Ni(OH)₂. Supplementary Fig. 11 gives the contrastive HADDF–STEM images of pristine and doped Ni(OH)₂ samples. Clearly, the W-doped sample gives many disordered sites in comparison with the typical symmetric hexagon structure of the pristine Ni(OH)₂ sample, further exemplifying that the W doping can change the lattice structure of Ni(OH)₂. For determining the mass ratio of W to Ni, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, aurora M90) was used. The atomic ratio was detected to be 2.985: 99.55, near the theoretical value (Supplementary Table 2).

**Electrocatalytic water oxidation performance.** The electrocatalytic activity of the Ni(OH)₂-r, w-Ni(OH)₂-e, and w-Ni(OH)₂ samples toward OER in a 1 M KOH aqueous solution was measured as shown in Fig. 4. As expected, the polarization curve of the w-Ni(OH)₂ sample gave the best catalytic activity among the three electrodes, delivering a much higher current density than the others at the same overpotential (Fig. 4a). Typically, all the Ni(OH)₂ samples showed the obvious Ni²⁺ ↔ Ni³/₄⁺ peak at the potential of ca. 1.45 V. Furthering the anodic potential, the control material pure Ni(OH)₂-r sample presented a slowly climbing line, indicating a gradual increase in current density. This was in contrast to the W-doped sample which showed a significantly steeper response at a lower potential. We next compared the overpotentials at three catalytic current density values of 10, 50, and 80 mA/cm² as shown in Fig. 4b. The w-Ni(OH)₂ electrode required an overpotential of 237 mV for reaching the current density of 10 mA/cm², where the reference samples of Ni(OH)₂-r and w-Ni(OH)₂-e required 351 and 264 mV, respectively. Note that the potential value of the control Ni(OH)₂-r sample at the current density of 10 mA/cm² was 351 mV, which is lower than those reported¹⁵,¹⁷–¹⁹. At a higher current density i.e., 80 mA/cm², the two samples of w-Ni(OH)₂-e and w-Ni(OH)₂ gave overpotential values of 290 and 257 mV, respectively. Please note that the W-doped thin layered Ni(OH)₂-i.e., w-Ni(OH)₂ showed the lowest overpotential at current densities of 50 and 80 mA/cm² amongst reported literature values of Ni(OH)₂-based OER catalysts (Supplementary Table 3). The kinetic parameters of the studied electrodes were further calculated from the corresponding polarization curves by plotting overpotential against log (j).

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**Fig. 2 Physicochemical property characterization. a** XRD patterns of the reference Ni(OH)₂-r, w-Ni(OH)₂-e, and w-Ni(OH)₂ samples; **b** UV–Vis absorption spectrum; **c** The W K-edge XANES spectra, and **d** the corresponding K²-weighted Fourier transform spectra of w-Ni(OH)₂, WO₃, and W powder were used as the reference samples.
showed Tafel slopes of 111, 58, and 33 mV/dec, respectively. To get a direct comparison, commercial RuO₂, a commonly used electrocatalyst for OER, was prepared and tested as shown in Supplementary Fig. 12, the overpotentials recorded were 350 and 470 mV at the current density values of 10 and 50 mA/cm², respectively. Moreover, the RuO₂ electrode gave a Tafel slope of 92 mV/dec.

It was thought that the higher intrinsic catalytic activity of w-Ni(OH)₂ may have been due to its higher conductivity over w-Ni(OH)₂-e or Ni(OH)₂-r. To confirm this hypothesis, EIS plots of the three samples were carried out as shown in Fig. 4d. According to the above detailed analysis of the EIS measurements (Fig. 1), the bias voltage was set to be 1.48 V. Clearly, the sample of Ni(OH)₂-r gave the biggest circular arc, followed by w-Ni(OH)₂-e and then w-Ni(OH)₂, suggesting that the W element doping improved the electrical conductivity which was then further improved by the exfoliation strategy. Supplementary Table 4 gives the corresponding fitted results based on the same equivalent electric circuit in Fig. 1c. Clearly, the Rₑ values show the rapid decrease from Ni(OH)₂-r to w-Ni(OH)₂, further confirming that the thin-layered W-doped sample had a relatively higher carrier mobility across the HL i.e., the catalyst|solution interface. Furthermore, chronopotentiotmetry experiments with multiple current steps were carried out to examine the rapid response of the carrier migration as shown in Fig. 4e. Attention was only paid to the relative high current density, which was increased from 50 to 100 mA/cm². The response change of applied potentials was answered by corresponding stable current values consistently, confirming the excellent carrier migration across the interface of the electrode and solution. Supplementary Fig. 13a gives the comparison of the activity between the initial surface and of the electrode surface was very important for OER. More analysis is needed to clarify the reaction sites of the single-atom W-doped material, w-Ni(OH)₂. According to Fig. 4a, the oxidation peaks of Ni²⁺ to Ni³⁺⁺⁺ at ca. 1.45 V show a slight positive shift for the W-doped samples. These results suggest that single-atom W doping can promote carrier migration across the catalyst|solution interface and weaken the oxidation step of Ni²⁺. The EIS plots (Fig. 4d) support this as the charge transfer.
resistance, $R_{ct}$ is significantly lower for w-Ni(OH)$_2$, see Table S4. The in situ Raman spectra of pristine and W-doped Ni(OH)$_2$ was carried out to further verify this. As shown in Supplementary Fig. 20, the Raman shift peaks at ca. 440 and 493 cm$^{-1}$ can be assigned to Ni(OH)$_2$ signals, meanwhile, the peaks at ca. 477 and 550 cm$^{-1}$ belong to the NiOOH. It was deduced that the Ni(OH)$_2$ was being oxidized to NiOOH, and the W-doped sample retained part of the Ni(OH)$_2$ phase. This directly correlates with our previous assertion, that the doped W can assist in the migration of carriers from the catalyst to solution and weaken the oxidation effect of the electrocatalyst Ni(OH)$_2$.

To better understand the effect of surface W sites on migrating carriers, the OER performance of the reference sample, i.e., WO$_3$/Ni(OH)$_2$ was also carried out. The STEM image (Supplementary Fig. 21a) clearly showed that the WO$_3$ nanoparticles were only loaded on the Ni(OH)$_2$ surface, not dispersed through it. Although the OER activity was a little enhanced by WO$_3$ loading (Supplementary Fig. 21b), the oxidation potential of the peak of Ni$^{2+}$ to Ni$^{3/4+}$ was almost the same. This indirectly suggests that the W doping could weaken the carriers stay on Ni(OH)$_2$. To further verify the advantage of our nanosheet sample, we also synthesized a nanoparticles sample of pure Ni(OH)$_2$. As shown in Supplementary Fig. 22, the nanosheet sample shows a better OER performance at high current density than the reference nanoparticle material. We also tried other element doping using Nb, Mo, and Ta, and the corresponding OER performance was shown in Supplementary Fig. 23. The doped samples all exhibited enhanced activity compared with the pure Ni(OH)$_2$ sample. However, their improved performance is limited in comparison with W element doping, suggesting that its unique electronic structure may be the reason for the enhanced performance. The specific activity of the samples is also an important parameter to suggest the intrinsic activity. The unit specific surface area values of the three catalysts (Ni(OH)$_2$-r, w-Ni(OH)$_2$-e, and w-Ni(OH)$_2$) were tested to be 45, 46, and 58 m$^2$/g, respectively. Supplementary Fig. 24 shows the corresponding specific activity. Clearly, the w-Ni(OH)$_2$ sample still gives the best performance.

To obtain more information regarding the water oxidation process, an electrochemically active surface area (ECSA) investigation of w-Ni(OH)$_2$ was carried out under the three pH values (pH = 13.6, 11, and 10). The characteristic CV curves of w-Ni(OH)$_2$ with different scan rates are shown in Supplementary Fig. 25a–c. By plotting the $\Delta j$ at a certain potential against the scan rate, a linear slope that is twice the double-layer capacitance ($C_{dl}$) can be obtained, and the $C_{dl}$ can be used to determine the corresponding ECSA. For our experiment, we used a potential of 1.45 V (vs. RHE) to obtain the ECSA, the results of which are given in Supplementary Fig. 23d. The slopes at pH =
LSV plots, but a little high current response in the high potentials.

The two-cell electrolyzer as shown in Supplementary Fig. 28. The OER activity. We also tried the practical water-splitting devices of deprotonation steps (State 2 and State 3) releasing energies of atom. Complete OER processes on the W-doped Ni(OH)2 and Ni molecules and then an edge Ni atom was substituted by a W (OH)2 sample under the three different pH conditions were responsible for a more electroactive surface. EIS plots of the w-Ni(OH)2 sample under the three different pH conditions were 100 times higher than the pristine Ni(OH)2, seen in Supplementary Fig. 26), followed by pH 13.6, 11, and 10 are 0.01, 0.0058, and 0.0042 mF cm\(^{-1}\), respectively. The W-doped sample shows a TOF (TOF) of Ni(OH)2-r and w-Ni(OH)2 were calculated to be 0.006 and 0.002, both of them were smaller than that of the w-Ni(OH)2 sample. This clearly suggested that the efficient property of the W-doped sample was the boosting of carrier migration across the electrode|solution interface. The turnover frequency (TOF) of Ni(OH)2-r and w-Ni(OH)2 were calculated to be 0.006 and 0.74 s\(^{-1}\), respectively. The W-doped sample shows a TOF 100 times higher than the pristine Ni(OH)2, seen in Supplementary Table 3, further confirming that the W doping can boost the OER activity. We also tried the practical water-splitting devices of the two-cell electrolyzer as shown in Supplementary Fig. 28. The corresponding OER performance shows the similar curves in the LSV plots, but a little high current response in the high potentials.

**W-doped Ni(OH)2 OER mechanism.** After the experimental characterization, density functional theory (DFT) calculations were implemented to unfold the microscopic mechanism of OER enhancement on W-doped Ni(OH)2. The six main sequential steps of water oxidation were explored:

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\begin{align*}
\text{H}_2\text{O} + \ast & \rightarrow \ast \text{H}_2\text{O} & (1) \\
\ast \text{H}_2\text{O} & \rightarrow \ast \text{HO} + \text{H}^+ + e^- & (2) \\
\ast \text{HO} & \rightarrow \ast \text{O} + \text{H}^+ + e^- & (3) \\
\ast \text{O} + \text{H}_2\text{O} & \rightarrow \ast \text{OOH}_2 & (4) \\
\ast \text{OOH}_2 & \rightarrow \ast \text{OOH} + \text{H}^+ + e^- & (5) \\
\ast \text{OOH} & \rightarrow \ast + \text{O}_2 + \text{H}^+ + e^- & (6)
\end{align*}
\]

where \(\ast\) represents the element of the surface reaction sites. The OER computational model (shown in Supplementary Fig. 29) adopted two layered a-Ni(OH)2 intercalated with Cl\(^-\) and H\(_2\)O molecules and then an edge Ni atom was substituted by a W atom. Complete OER processes on the W-doped Ni(OH)2 and Ni(OH)2 were shown in Fig. 5, in which the six reaction steps involved four electron–proton combinations\(^43\). In the case of w-Ni(OH)2 (Fig. 5a), one water molecule was adsorbed on the exposed W\(^6\) site (State 1), and then proceeded through two deprotonation steps (State 2 and State 3) releasing energies of 0.76 eV and 0.34 eV, respectively. The adsorbed O radical then attracted one water molecule (State 4) and required 1.31 eV reaction free energy to proceed. After that, the adsorbed H\(_2\)O molecule participated in O–O coupling to form \(\ast\)OOH (State 5) with a near-zero free uphill energy requirement. Please note that this step was different from the case of Fe-doped Ni oxyhydroxides (Ni\(_{1-x}\)Fe\(_x\)OOH), which are considered as the current most active non-noble electrolytcatls for OER under alkaline conditions and prefer the O–O coupling to occur at the low spin d\(^0\) Ni\(^{2+}\) rather than at high spin d\(^1\) Fe\(^{3+}\)\(^{54}\). Whereas the low spin d\(^0\) W\(^6\) stabilized the unpaired electron of the O and then assisted in the formation of O–O coupling. The above adjacent two steps did not then need to change their reactive sites and thereby the energy requirement was reduced. For the last step, the \(\ast\)OOH had to overcome a 1.67 -eV free energy barrier to achieve deprotonation into the O\(_2\) molecule (State 6), and consequently, the last step in the W-doped system is the Potential Determining Step (PDS) for OER. The overpotential was obtained based on the above results by subtracting the thermodynamic equilibrium potential (1.23 V for OER) from the highest free energy (1.67 eV) required for OER: \(\eta = 1.67\, \text{eV} / \text{e} - 1.23\, \text{V} = 0.44\, \text{V}\). Moreover, the spin states were also examined for the different states of the metal and intermediates as given in Table S6. Clearly, when compared with the high spin population (1.434) of Ni atom, a lower spin state of W atom was responsible for the stabilization of O–O bonding formation as discussed by Shin, Xiao, and Goddard\(^54\). As a contrast, in the case of pure Ni(OH)2, the first four states are all a result of endothermic reactions as shown in Fig. 5b, and step 4, the formation of \(\ast\)OOH\(_2\) is the PDS, which requires an uphill energy of 2.32 eV with a corresponding \(\eta\) of 1.09 V. Furthermore, the O radical on Ni\(^{3+}\) was hard to form from State 3 to State 4, which induced an instability of O radical adsorption. The O–O–H formation (State 5) was an exothermic step and the final O–O coupling step needed an energy of 0.66 eV. The W-doped configurations, compared with bare Ni(OH)2, with a low spin population of 0.05 for the W atom showed it could stabilize the subsequent O–O coupling. As a result, the potential determining step of O radical formation on bare Ni(OH)2 is transferred to the deprotonation of \(\ast\)OOH. Also, the W element doped Ni(OH)2 sample gave the smallest overpotential at a relatively high current density of 80 mA/cm\(^2\) over all the Ni(OH)2-based OER catalysts in the literature. We also tried other dopant sites for W as shown in Supplementary Fig. 30. It was found that at the edge site, the dopant W is more energetically favorable than that of the interior W configuration. Note that although the PBE results cannot reproduce the exact experimental redox potentials due to the effect of the exchange-correlation functional in Ni oxyhydroxides systems, previous work showed that it has little influence on the knowledge of the concrete OER, especially at the PDS\(^55\). The K-point test of w-Ni(OH)2 systems for DFT calculations were carried out as shown in Supplementary Fig. 31. Meanwhile, we compared the dynamic processes of the PDS on w-Ni(OH)2 and Ni(OH)2 as shown in Supplementary Fig. 32. It was found that a lower kinetic energy barrier (2.05 eV) of the PDS on w-Ni(OH)2 was needed to be overcome when compared with that of PDS on pristine Ni(OH)2 (2.29 eV), meaning a faster electron transfer occurrence at this elementary step of OER. It agreed well with the steeper current response at low potential observed in the experiment.

**Discussion**

In summary, single-atom W-doped Ni(OH)2 nanosheets were reported for the electrocatalytic water oxidation reaction. The w-Ni(OH)2 was synthesized from long-time ultrasonic exfoliation of w-Ni(OH)2-e, which was obtained via an alcoholothermal method. Compared with the reference sample of pure layered Ni(OH)2, w-Ni(OH)2 gave an obvious enhanced OER performance: it only required an overpotential of 237 mV for reaching the current density of 10 mA/cm\(^2\). Moreover, at a high current density of 80 mA/cm\(^2\), the sample of w-Ni(OH)2 only needed a overpotential value of 267 mV with the corresponding Tafel slope measured to be 33 mV/dec. All the values were the best/highest level with respect to the current reported samples in the literatures. Based
on DFT calculations, the w-Ni(OH)₂ showed exothermic reactions for the first three steps of water oxidation: water adsorption, the formations of adsorbed OH− group and the O radical. The site of d⁰ W⁶⁺ stabilized the O radical owing to the low spin population of 0.05. Most significantly, the following O−O coupling step was also generated at the W⁶⁺ site, and almost-zero eV of the Gibbs free energy was further required. This effect helped the W⁶⁺ ions boost the final water oxidation reaction of Ni(OH)₂. This work can help us understand the effect of the HL on the water oxidation and provide a new direction to design doped OER catalysts.

Methods

Synthesis of pure Ni(OH)₂-r. The Ni(OH)₂ was prepared through an alcohothermal method. Typically, 0.4 g of NiCl₂ was added into a 40 -mL ethanol solution. The mixture was stirred until a transparent solution was observed. The solution was then moved into a 50 -mL autoclave. The autoclave was then placed into an oven and treated in flowing air and heated at 150 °C for 12 h. Green powder of Ni(OH)₂ was treated by 24 h ultrasound in an ethanol solution and then was collected by centrifuging the reaction mixture at a speed of 9000 r.p.m. for 10 min. The product was washed by water and ethanol four times and then dried at 80 °C overnight. The obtained pure Ni(OH)₂ was used as the reference sample and named as Ni(OH)₂-r.

Synthesis of w-Ni(OH)₂-e. The w-Ni(OH)₂-e was prepared through an alcohothermal method. At first, 1 g of WCl₆ was added into 100 mL of ethanol to form a transparent solution. Then a certain amount of WCl₆-ethanol solution (0.4g-40mL) by a pipette. After stirring for 15 min, the mixture was moved into a 50 -mL autoclave, which was then treated at 150 °C for 12 h in an oven. The product was collected by centrifuging the reaction mixture at a speed of 9000 r.p.m. for 10 min. After that, the powder was washed by water and ethanol four times and then dried at 80 °C overnight. The obtained W-doped Ni(OH)₂ sample was named as w-Ni(OH)₂-e.

Synthesis of w-Ni(OH)₂. The w-Ni(OH)₂ was prepared through the exfoliation of the w-Ni(OH)₂-e sample. Typically, 0.1 g of w-Ni(OH)₂-e was added into 40 mL of ethanol and then the mixture was treated by ultrasound for 24 h. After that, the product was collected by centrifuging at a speed of 9000 r.p.m. for 10 min. The powder was washed by water and ethanol four times and then dried at 80 °C overnight. The obtained sample was named as w-Ni(OH)₂.

Structural characterization. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 F20 electron microscope at an acceleration voltage of 200 kV. Spherical aberration-corrected electron microscopy was carried out on a JEM-ARM200F electron microscope. The field-emission scanning electron microscopy (FESEM) was observed under a SU8020 electron microscopy. X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku Smartlab-9KW instrument using Cu Ka X-ray (λ = 1.54186 Å) radiation at a scanning rate of 4°/min in the region of 20 = 10–80°. X-ray photoelectron spectra (XPS) was acquired on a Kratos Axis Ultra DLD spectrometer with Al Ka (hv = 1486.6 eV) as the excitation source. Fourier transform infrared reflectance (FTIR) and the Quasi FTIR spectra of samples were carried out on a Bruker V70 spectrometer. Diffuse reflectance ultraviolet–visible (UV–Vis) spectra of the studied samples were recorded in the air against BaSO₄ in the region of 200-800 nm on a Perkin–Elmer Lambda 950 spectrophotometer. Raman analysis was carried out on a Renishaw InVia Raman spectrometer with a green line of an Ar-ion laser (514.53 nm) in micro–Raman configuration. XAFS experiments were performed at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF). The storage ring runs at 2.0 GeV with a maximum electron current of about 450 mA. The energy range of the incident X-ray is tunable from 4 to 25 keV by fix-exit Si (111) double-crystal monochromator. The absorption edge of standard metal foils was used to calibrate the X-ray energy. Samples were ground into fine powders and then pressed into thin disks of 10 mm in diameter. W L3-edge XANES/EXAFS spectra were collected at room temperature in transmission mode. The data were processed using the IFEFFIT package56.

OER electrode preparation. For the three samples studied and the reference RuO₂, the preparation method was the same. Typically, 10 mg of the sample was added into a 50 μL of isopropanol and then 50 μL of nafion (Nafion 117 solution, Sigma-Aldrich) was dispersed into the solution. The mixture was treated by ultrasound ca. 10 h to form the uniform ink, which was then dropwise applied onto glassy carbon electrodes with a mass loading of 0.2 mg cm⁻². The prepared electrodes were naturally dried in air. For all the samples, four electrodes were prepared and the near results were used in our paper.

Electrochemical characterizations. All of the electrochemical tests were performed at room temperature with the use of a typical three-electrode setup. The Pt (1 cm²) and Hg/HgO (1 M KOH) electrodes were used as the counter and reference electrodes, respectively. In all, 1 M KOH solution was used as the electrolyte. The electrocatalytic measurements were carried out on a Zennium Zahner electrochemical workstation. The measured potentials versus Hg/HgO were converted to the reversible hydrogen electrode (RHE) scale according to the following Nernst equation: $E_{RHE} = E_{Hg/HgO} + 0.059 pH + E^°_{Hg/HgO}$, where $E_{Hg/HgO}$ is the converted potential versus RHE, $E^°_{Hg/HgO}$ is 0.098 at 25 °C, and $E^°_{Hg/HgO}$ is the experimentally measured potential against the Hg/HgO reference. Before the test, the as-prepared anodes were activated by a chronopotentiometry scan with the 30 mA cm⁻² current density for 2 h. The Tafel slopes were obtained from the polarization curves by plotting overpotential against log(current density). The steady-state activity was evaluated by chronopotentiometry measurements under different potentials. The
ECSA was determined by measuring the capacitive current associated with double-layer charging from the scan rate CV-dependence. In our present work, the CV potential sweep was chosen to be 1.35 to 1.55 V vs. RHE. The scan rates were 20, 40, 60, 80, and 100 mV s\(^{-1}\). The double-layer capacitance \(C_{dl}\) was estimated using the equation: \(\Delta V = \frac{1}{2C_{dl}}\). The scan rate CV-dependence. In our present work, the CV potential sweep was chosen to be 1.35 to 1.55 V vs. RHE. The scan rates were 20, 40, 60, 80, and 100 mV s\(^{-1}\). The double-layer capacitance \(C_{dl}\) was estimated using the equation: \(\Delta V = \frac{1}{2C_{dl}}\).

The data that support the findings of this study are available on request from the corresponding authors.

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Author contributions
J.Y. and T.M. planned and designed the experiments, J.Y. and L.K. performed and analyzed the data, and wrote the paper. S.-Z.L. supervised the project, S.-T.L. and J.W. discussed the results. Y.I. and Y.L. performed the DFT calculations. P.A. and I.Z. performed and analyzed the XANES and EXAFS experiments. All authors discussed the results and commented on the paper.

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