

# Ir-O-V Catalytic Group in Ir-Doped NiV(OH)<sub>2</sub> for Overall Water Splitting

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**S** Supporting Information

ABSTRACT: Bifunctional electrocatalysts for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are very crucial for converting water into clean fuel through overall water splitting. Here, we report on a bifunctional catalyst based on Ir-doped NiV layered double hydroxide with Ir-O-V catalytic groups on which water dissociation, HER, and OER occur on Ir, bridge O, and V atoms, respectively. Interestingly, the dopant Ir ions were found to play a triple role: (i) serve as catalytic sites for water dissociation, (ii) reduce charge density on adjacent bridge oxygen, thus facilitating HER there, and (iii) increase charge density on V ions, which in turn boosts OER. As a result, the catalyst achieves an ultralow applied voltage for overall water splitting (1.49 V @ 10 mA cm<sup>-2</sup>) and beats the noble metallic couple Pt/C and Ir/C with its value of 1.60 V @ 10 mA cm<sup>-2</sup>.



lectrolysis of water is known as an effective way to convert electricity into clean hydrogen energy,<sup>1,2</sup> for ✓ which highly efficient catalysts are actively sought to accelerate both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).<sup>3,4</sup> To date, the predominant HER and OER catalysts are based on precious metals and their oxides (e.g., Pt/C for HER and  $RuO_2$  for  $OER^{5-9}$ ), while the scarcity and high costs seriously restrict their practical applications.<sup>8,9</sup> Ni-based LDHs have long been known as promising OER catalysts<sup>10-12</sup> whose performance can be further improved by doping with V ions.<sup>13,14</sup> However, Ni-based LDHs were reported to display appealing HER performance after being doped or forming heterojunction.<sup>15–18</sup> Thus, Ni-based LDHs show great potential as both anode catalyst for OER and cathode catalyst for HER, being eventually capable of driving overall water splitting under a low working potential.<sup>16–19</sup>

In principle, an ideal OER catalyst should possess a moderate adsorption energy for the  $O^{\ast}$  intermediate,  $^{19,20}$  while an ideal HER catalyst adsorbs the H\* intermediate appropriately.<sup>21</sup> Previous studies suggested that metal ions in LDHs serve as both HER and OER catalytic sites.<sup>15,22</sup> In this scenario, it is impossible to achieve an optimal adsorption of O\* and H\* species simultaneously on the same active site due to the distinct electronegativity of the two intermediates.<sup>23</sup> Indeed, while Nibased LDHs were purposely designed for a certain application (either HER or OER), there is still a big room to improve their performance for both HER and OER. Consequently, the overall

water splitting in the presence of Ni-based LDHs proceeds at rather high values of applied voltage, usually larger than 1.55 V.<sup>24–26</sup> At the same time, little research was undertaken to date aiming at engineering bifunctional LDH catalysts, i.e., those combining simultaneously optimized adsorption of HER and OER intermediates.

Herein, we aimed at designing separate catalytic sites for HER and OER on the surface of Ni-based LDHs, so that the H\* and O\* intermediates could be adsorbed by such sites and adjusted independently. More specifically, we considered oxygen and metal ions as HER and OER catalytic sites, respectively, because the exposed oxygen atoms are known to capture H\* intermediates and metal cations are attractive for O\* intermediates. In light of this, we selected NiV LDH as the starting material and introduced iridium dopant to construct Ir-O-V catalytic groups in which Ir atoms were to help dissociate water molecules and adjust the adsorption energies of bridge oxygen and V atoms. The resultant NiVIr LDH exhibited excellent performance with the OER and HER overpotential values of 203 and 41 mV@10 mA cm<sup>-2</sup>, respectively. Thereby, the newly prepared NiVIr LDH catalyst achieved an overall water splitting current of 10 mA cm<sup>-2</sup> under an applied voltage of 1.49 V (as both anode and cathode), which is much lower

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Figure 1. Active sites (top) in the overall water splitting process and differential-charge densities (down) of (a) NiV LDH and (b) NiVIr LDH. For active site structures, light gray/dark gray, light red/dark red, blue, green, and white balls represent V/active V sites for OER, O/active O sites for HER, Ni, Ir, and H atoms, respectively. Orange balls stand for O in water involved in the splitting process. For differential-charge densities of NiV LDH and NiVIr LDH, yellow and blue regions represent excess and depletion of charge density, respectively. The isosurface value is 0.018 eÅ<sup>-3</sup>.



Figure 2. (a) Surface morphology (SEM image) of NiVIr catalyst. (b) XRD patterns of as-prepared  $Ni(OH)_2$  (purple), NiV LDH (blue), and NiVIr LDH (orange). (c, d) Narrow scan XPS spectra of Ni (c) and V (d) in NiV LDH and NiVIr LDH.

than that of the Pt/C–Ir/C couple ( $1.60 \text{ V} @ 10 \text{ mA cm}^{-2}$ ) and appeared to set up a new record for overall water splitting. The present work demonstrates a conceptually new catalytic group with significantly higher performance, which opens up new avenues toward next-generation bifunctional electrocatalysts for overall water splitting.

In order to verify the above assumption, we first screened the possible catalytic sites for HER and OER in NiV LDH and NiVIr LDH by calculating the Gibbs free energy (Figure S3). The corresponding slab models for NiV LDH and NiVIr LDH are presented in Figure S1 and Figure S2, respectively. Commonly, metal atoms are known to combine the roles of HER and OER catalytic sites on the surface of LDHs. However, the situation changes dramatically in the case of NiV LDH. As clearly seen in Figure S3a, the bridge oxygen atom located between those of Ni and V shows a lower HER energy barrier (0.44 eV) than those of vanadium (0.46 eV), nickel (1.18 eV), and bridge oxygen between two Ni atoms (1.36 eV). This suggests that doping with vanadium properly modifies the ability of bridge oxygen atoms to absorb hydrogen and makes them active sites for HER.



Figure 3. OER and HER activity of prepared samples  $(Ni(OH)_2, NiV)$ , and NiVIr) and their comparison with conventional counterparts. (a) Polarization curves and (b) corresponding Tafel plots of as-prepared catalysts and Ir/C. (c) Polarization curves and (d) corresponding Tafel plots of as-prepared catalysts and Pt/C.

However, vanadium atoms are favorable for adsorption of OER intermediates and are seen to provide an OER energy barrier of 1.47 eV, which is much lower than that of nickel atoms (2.67 eV) (see Figure S3b). Therefore, in the case of NiV LDH, HER and OER are expected to occur preferentially on bridge oxygen and vanadium atoms, respectively, as indicated in Figure 1a. Nevertheless, the overpotential values for this material are still high (0.44 eV for HER and 0.24 eV for OER) due to excessively tight adsorption of intermediates of HER and OER.

Next, we investigated the effect of Ir doping on catalytic properties of NiV LDH. As shown in Figure 1b, after one nickel atom was substituted by iridium, an obvious decrease in charge density was observed on the bridge oxygen atom located between vanadium and iridium atoms. Correspondingly, the valence state of the bridge oxygen decreases from -1.08 in the NiV LDH to -0.94 in the NiVIr LDH material according to the Bader charge analysis. Hence, the excessively strong adsorption of hydrogen intermediates observed on bridge oxygen of the NiV LDH could be reduced. However, doping with iridium is seen to lead to an increase in charge density on vanadium atoms, thus reducing the excessive adsorption of OER intermediates. In brief, doping with iridium is expected to boost both HER and OER performance of the novel NiVIr LDH simultaneously.

To test the above hypothesis, we prepared three samples, namely, pure Ni hydroxide,  $Ni_{0.71}V_{0.29}$  LDH, and  $Ni_{0.57}V_{0.29}Ir_{0.14}$ LDH (denoted as Ni(OH)<sub>2</sub>, NiV-LDH, and NiVIr-LDH, respectively), through a one-step hydrothermal process. The ratios of metal ions present in each sample were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; see Supporting Information Table 1) and confirmed by energy dispersive X-ray spectroscopy (EDS; see Supporting Information Figure S4). Morphologically, all three samples were similar, being composed of nanosheet arrays grown vertically on nickel foam, as revealed by scanning electron microscopy (SEM) images shown in Figure 2a and Figure S5. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) images illustrate that each nanosheet in the NiVIr LDH sample is several hundred nanometers in size and 6 nm thick (see Supporting Information Figure S6 and Figure S7). X-ray diffraction (XRD) patterns in Figure 2b and Figure S8 indicate that the NiV LDH and NiVIr LDH samples possessed the same phase structure as  $\alpha$ -Ni(OH)<sub>2</sub> (JCPDS card no. 38-0715),<sup>13,14,34</sup> and no extra diffraction peaks are observed, indicating single-phase composition of the three samples. The (003) and (006) peaks of the NiVIr LDH sample are seen in Figure 2b to be shifted slightly to lower values by ~0.3° in comparison with the other samples, which implies that the introduction of larger Ir ions into NiV LDH caused a lattice expansion.

The valence state and electronic structure of the LDH samples were investigated by X-ray photoelectron spectroscopy (XPS) (see Figure 2c,d and Supporting Information Figure S9). For NiV LDH, the Ni 2p spectrum could be well fitted by two Gaussian peaks with binding energies at 855.4 and 872.9 eV, along with two satellites (Figure 2c), which are characteristic of Ni<sup>2+</sup> ions. The V 2p 3/2 peaks were deconvoluted into three peaks (Figure 2d) located at 516.2, 516.9, and 517.5 eV, which belong to V<sup>3+</sup>, V<sup>4+</sup>, and V<sup>5+</sup> ions, respectively.<sup>13,14</sup> For NiVIr LDH, Ni ions keep the same valence state (+2) as in NiV LDH, while its V 2p peaks were found to be shifted to lower binding energy by 0.3 eV and the peak area of  $V^{3+}$  ions increased significantly, indicating that the valence state of V ions in the Irdoped sample decreases in comparison with its nondoped counterpart. This finding is also verified by electron energy loss spectroscopy (EELS). As shown in Figure S10, after doping with Ir, both L3 and L2 peaks of V ions are negatively shifted (see orange spectrum in Figure S10), which can be ascribed to a decrease in chemical valence.<sup>27,28</sup> Moreover, the XPS Ir 4f peaks of the doped LDH located at 65.6 and 62.6 eV are attributed to

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Figure 4. (a) Polarization curves of NiV LDH, NiVIr LDH, Pt/C-Ir/C couple, and NiFe LDH-Ir/C couple for overall water splitting. (b) Comparison of the novel catalyst with other bifunctional electrocatalysts used for overall water splitting in 1 M KOH at a current density of 10 mA cm<sup>-2</sup>. (c) Chronoamperometric responses of NiVIr LDH catalyst, Ir/C-Pt/C couple, and NiFe LDH-Ir/C couple at a current density of 10 mA cm<sup>-2</sup>. (d) HER (orange curve) and OER (green curve) overpotentials of NiVIr LDH catalysts with different Ir contents at a current density of 10 mA cm<sup>-2</sup>.

 $Ir^{3+}$  species (see Supporting Information Figure S9c), indicating that the oxidation state of Ir ions in this sample is +3.<sup>29</sup>

The HER performance of the above catalysts was assessed in N2-saturated 1 M KOH electrolyte using a standard threeelectrode setup with a graphite rod as the counter electrode. The Ir-doped LDH sample was found to exhibit an outstanding HER activity, which was evidenced by an ultralow overpotential of 41 mV at 10 mA cm<sup>-2</sup>. For comparison, the overpotential of the nondoped LDH measured at 10 mA cm<sup>-2</sup> was up to 148 mV (Figure 3c). The Tafel slope of the doped LDH was as low as 35.9 mV dec<sup>-1</sup>, being comparable with that of Pt/C (32.8 mV  $dec^{-1}$ ) (Figure 3d). Moreover, as clearly seen in Figure S11, the turnover frequency (TOF) of the NiVIr LDH sample observed at an overpotential of 150 mV was up to  $0.028 \text{ s}^{-1}$ , which is more than 7-fold higher than that of the NiV LDH. In addition, the Irdoped sample demonstrates high long-term durability, as its overpotential at 10 mA cm<sup>-2</sup> was found to rise slightly (by 4 mV) after 2000 cycles of CV scans at a scan rate of 50 mV s<sup>-1</sup> (see Supporting Information Figure S12a). Besides, after 10 h of testing at 10 mA cm<sup>-2</sup>, its overpotential increased just by 21 mV, as seen in Figure S12b. After the durability tests, both the morphology and phase composition of the sample remained unchanged, thus indicating the superior stability of the newly developed catalyst (Figure S13).

Next, the OER activities were evaluated in a typical threeelectrode system where the as-prepared catalyst, platinum electrode, and Hg/HgO electrode serve as the working electrode, counter electrode, and reference electrode, respectively. To exclude the influence of trace Fe ions, the electrolyte (O<sub>2</sub>-satured 1 M KOH) was purified by following a well-proved procedure previously reported in the literature.<sup>30–32</sup> The liner sweep voltammograms (LSVs) presented in Figure 3a illustrate that the Ir-doped LDH (orange curve) exhibit a low overpotential of 203 mV to achieve a current density value of 10 mA cm<sup>-2</sup>, which is superior to those for the Ni(OH)<sub>2</sub> (337 mV, purple curve), NiV LDH (319 mV, blue curve), and even commercial Ir/C (284 mV, gray curve). Figure 3b exhibits that the Tafel slope of the Ir-doped LDH is as low as 55.3 mV dec<sup>-1</sup>, which is much lower than 119.2 mV dec<sup>-1</sup> recorded for its nondoped counterpart, as well as 86.8 and 214.1 mV dec<sup>-1</sup> detected for the Ir/C and Ni(OH)<sub>2</sub> samples, respectively. In addition, the TOF value of the newly designed catalyst (0.0157 s<sup>-1</sup> at overpotential 250 mV) was found to be almost 11-fold larger than that of nondoped Ni<sub>0.71</sub>V<sub>0.29</sub> (0.0014 s<sup>-1</sup>), which also confirms its excellent catalytic activity (Figure S14).

It is clearly seen in Figure S15a that the NiVIr LDH sample also displayed good durability as after 2000 cyclic voltammetry (CV) scans at a scan rate of  $50 \text{ mV s}^{-1}$  its overpotential at 10 mA cm<sup>-2</sup> increased by only 4 mV. A long-term electrocatalytic OER testing performed at 10 mA cm<sup>-2</sup> demonstrates an increase in overpotential by only 19 mV over a period of 10 h (Figure S15b). At the same time, the elemental composition and morphology of the novel LDH catalyst were found to be maintained after the above durability tests, and only XPS Ni 2p and V 2p spectra show slight shifts to higher binding energy, implying gradual deeper oxidation of the elements during longlasting OER procedures (see Supporting Information Figure S16). The Ir 4f spectrum signals taken ex situ prove that the of Ir<sup>3+</sup> species remain stable after the OER test.<sup>29</sup> The stability of Ir<sup>3+</sup> observed in the structure of NiVIr LDH may arise from its ionic radius similar to that of Ni<sup>3+</sup>.

The compositional changes in the catalysts during OER testing were traced by using inductively coupled plasma optical emission spectrometry (ICP-OES). Both the NiV and NiVIr

LDHs were found to suffer some loss of V ions, especially at the beginning of OER test (Table S2). For the NiV LDH, the loss of V atoms increased with the number of CV cycles, which led to 37.9% remaining after 300 CV cycles. At the same time, the loss of V atoms in the NiVIr LDH was much weaker than that in the NiV LDH, becoming negligible after 50 CV cycles. Thus, Ir doping was found to enhance the elemental stability of the catalyst.

It is known that the presence of trace Fe ions in the electrolyte can influence OER catalytic performance significantly. To investigate the effect of trace Fe, we conducted the Fe-spiking experiment in the electrolyte contain 1 M KOH and 0.1 mM Fe(NO<sub>3</sub>)<sub>3</sub>.<sup>30</sup> For the NiV LDH, a significant improvement of OER activity was observed upon adding Fe<sup>3+</sup> ions (Figure S17a and Figure S17b), the finding being similar to what was previously observed for a NiO<sub>x</sub>H<sub>y</sub> catalyst.<sup>30–32</sup> In contrast, the NiVIr LDH did not show any dramatic changes in its OER properties in the presence of Fe<sup>3+</sup> ions (Figure S17c and Figure S17d). According to the results of XPS (Figure S18) and ICP-OES (Table S3) analyses, Fe ions were not incorporated into the novel catalyst, which is different from previous reports for NiO<sub>x</sub>H<sub>y</sub> catalysts and can explain why the NiVIr material is insensitive to trace Fe ions.

Encouraged by the above-mentioned high HER and OER activities of the novel catalyst, we tested it as the anode and cathode for catalyzing overall water splitting. As shown in Figure 4a, an extremely low cell voltage of 1.493 V was required to obtain a current density of 10 mA cm<sup>-2</sup>. This voltage is much lower than those achieved by a NiFe LDH-Ir/C couple(1.547 V), Ir/C-Pt/C couple (1.597 V), as well as the recently reported Ni-based bifunctional or LDH structures, such as NiFeRu (1.52 V),<sup>15</sup> Cu@NiFe-LDH/CF (1.54 V),<sup>18</sup> NiCoFe-LTH/CFC (1.55 V),<sup>33</sup> or NiFeV-LDH(1.59 V).<sup>34</sup> The Faradaic efficiency (FE) of the NiVIr LDH as bifunctional electrocatalyst for overall water splitting was determined to be about 99% (see Supporting Information Figure S19). As the two-electrode device was driven by a 1.5 V solar cell, the evolution of gas bubbles could be clearly observed on both electrodes (Figure 4c, inset, and Figure S20). This again confirms the high activity of the novel catalyst toward overall water splitting (see Figure 4b and Table S4). In addition, the Ir-doped material demonstrated very stable water splitting behavior at 10 mA  $\rm cm^{-2}$  for over 15 h, which was better than the results of the NiFe LDH-Ir/C couple and Ir/C-Pt/C couple (Figure 4c).

Further, we varied the concentration of Ir dopant in the NiVIr LDH material to investigate its influence on structure and performance. A series of Ir-doped LDHs with different Ir contents were obtained by adjusting the amount of IrCl<sub>3</sub> added during synthetic process. ICP-OES results indicated that Ni content decreased along with increase in Ir content, while the V content remained stable. This suggests that Ir atoms entered the lattice of NiV LDH by substituting Ni atoms (Table S5). Once the Ir content exceeded 19%, the flake-like morphology of the product decayed, turning into separate nanoparticles (see Supporting Information Figure S21). At the same time, the crystal structure was found by XRD to collapse and become amorphous (see Supporting Information Figure S22). The electrochemical active surface areas (ECSA) of different samples were assessed by measuring their electrochemical double layer capacitance (Cdl), as shown in Figure S23. The results demonstrated that doping with Ir significantly improves samples' Cdl and ECSA, leading to active surface area values as high as 30.38 mF cm<sup>-2</sup> (for  $Ni_{0.57}V_{0.29}Ir_{0.14}$  LDH), which is

more than 2 times that of NiV-LDH (13.1 mF cm<sup>-2</sup>). As shown in Figure 4d, both HER and OER performance first increased and then decreased with the increase in Ir content, resulting in the best overpotential, Tafel slope and charge-transfer capability for both HER and OER achieved at composition  $Ni_{0.57}V_{0.29}Ir_{0.14}$ (see Supporting Information Figures S24 and S25).

Finally, systematic DFT+U calculations were carried out on both nondoped and Ir-doped LDHs to reveal further the effect of Ir doping. In alkaline solutions, water dissociation and H adsorption are known as the key factors for HER and hydrogen evolution. Of all possible catalytic sites for water dissociation on NiV LDH, it is the V atoms that exhibit the lowest energy barrier of transition state (0.15 eV) (Figure 5a). Meanwhile, in the case



Figure 5. (a) Transition barrier for  $H_2O$  dissociation on surface of NiV and NiVIr LDHs, with V and Ir ions being active sites for water adsorption in NiV and NiVIr, respectively. (b) Gibbs free energy of H adsorption on surface of NiV and NiVIr LDHs. (c) Gibbs free energy of proposed 4e<sup>-</sup> mechanism for oxygen evolution reaction on the surface of NiV and NiVIr LDHs obtained from DFT+U calculations, with V ions being active sites in both structures. Blue and orange lines present results for NiV and NiVIr LDHs, respectively.

of the Ir-doped sample, the energy barrier of Ir atoms is 0.38 eV, being lower than that of V atoms, 0.44 eV (Figure S26), which makes Ir atoms more attractive sites for water dissociation (Figure 5a). Note that the energy barriers of both the NiVIr LDH and NiV LDH catalysts are lower than that of Pt/C (1.03 eV) which is the best known HER catalyst.<sup>35</sup> Therefore, the water dissociation step is not the rate-determining step (RDS) for the two catalysts.

As for the H adsorption, the formal calculation shown in Figure S3 revealed that the bridge oxygen in the NiV LDH is especially apt for H adsorption. Detailed calculations indicated that the bridge oxygen displays an adsorption energy of -0.44 eV, which makes hydrogen desorption rather difficult (Figure Sb). For comparison, Ir doping lowers the adsorption energy on adjacent oxygen to just -0.03 eV, thus making the NiVIr LDH an excellent catalyst for HER (Figure Sb). Moreover, the electric conductivity of NiVIr LDH was investigated by correlating the capacitance and mass loading. The latter mass loading was determined by integrating the Ni<sup>2+/3+</sup> redox wave (Figure S27).

The electrode capacitance (Figure S28) was found to increase linearly with mass loading (Figure S29), indicating that the NiVIr catalyst is conductive and can work under cathodic conditions.<sup>36</sup>

Regarding OER, the widely accepted pathway involves a four step proton-electron transfer which starts with the adsorption of OH<sup>-</sup> from the alkaline solution, followed by the formation of \*O, \*OOH, and \*O<sub>2</sub> intermediates.<sup>37,38</sup> We screened all possible active sites on the surface of both the NiV LDH and NiVIr LDH and found that V atoms are the most favorable adsorption and catalytic sites in both cases (Figure S3b and Figure S30b). In addition, the calculation based on the density of states (DOS) theory indicated that Ir doping lowers the d-band center of V atoms remarkably (Figure S31), which in turn weakens the adsorption of OER intermediates on V atoms, according to the d-band center theory.<sup>13,39,40</sup> The optimized adsorption energy of V atoms achieved in the newly developed catalyst is very advantageous for lowering the thermodynamic barrier of the RDS,  $O^* + OH^- \rightarrow OOH^* + e^-$ . As shown in Figure 5c, after doping with Ir atoms, the energy barrier reduces from 1.47 eV in NiV LDH to 1.38 eV in NiVIr LDH. Correspondingly, the total OER overpotential of the NiVIr LDH could be reduced by 90 mV, which agrees well with our experimental results.

On the basis of the above calculations, we can conclude that in the Ir-O-V group each atom plays an indispensable role for overall water splitting. More specifically, Ir serves as active site for water dissociation and optimizes the adsorption energy of O and V neighbors, while the latter O and V atoms act as active sites for HER and OER, respectively. Altogether, all this permits to boost the HER and OER performance of the novel catalyst.

As a summary, we engineered a novel bifunctional catalyst consisting of surface Ir-O-V groups that are extremely efficient for overall water splitting. The as-prepared NiVIr LDH exhibits excellent catalytic properties with OER overpotential of 203 mV at 10 mA cm<sup>-2</sup> and HER overpotential 41 mV at 10 mA cm<sup>-2</sup>. When used as both anode and cathode for overall water splitting, the new material required an extremely low applied voltage of 1.493 V to obtain a current density of 10 mA cm<sup>-2</sup>, thus outperforming the noble metallic Pt/C–Ir/C couple. Comprehensive characterizations and DFT+U calculations indicated that the surface Ir-O-V groups provide catalytic sites necessary for water dissociation, HER and OER processes. More specifically, their Ir, O, and V atoms controllably modify the electronic structure and adsorption energies of both water molecules and then intermediates to appropriate values, thus significantly decreasing the HER and OER overpotentials. Our work demonstrates that mild doping with noble metals is an effective strategy to improve the catalytic performance of layer double hydroxides, which boosts their efficiency and reduces the consumption of expensive metals.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergy-lett.9b01252.

Experimental details and computational methods, physical characterization data, and schematic presentations of hydrogen and oxygen evolution reactions, H adsorption energy on all possible active sites and Proposed 4e<sup>-</sup> mechanism of oxygen evolution reaction, EDS spectra and element ratios, SEM, TEM, and AFM images, XRD patterns, XPS and EELS spectra, HER data, polarization curves, mapping images, TOF LDHs, stability test, CV curves, amount of gaseous products for the watter splitting, photograph of a two-electrode configuration, Cdl calculations, Tafel plots, EIS analyses, HER and OER performances, water dissociation barrier, integration of Ni reduction wave for determining mass loading, capacitance as a function of mass loading, TDOS and PDOS, tables of composition data, water splitting activities adsorption energies, and Gibbs free energies and overpotentials (PDF)

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#### Notes

The authors declare no competing financial interest.

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