

Electronic Supporting information for Trace tungsten and iron-doped nickel hydroxide nanosheets for an efficient oxygen evolution reaction

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Calculation

Equation S(1) XRD Williamson-Hall methods

We could get the information about lattice strain and crystalline size based on Williamson-Hall equation through the full width at half maximum (FWHM) of the XRD peak. The W-H equation is (1),

$$\frac{\beta_{hkl} \cos \theta}{\lambda} = \frac{k\lambda}{D} + 4\varepsilon \sin \theta \quad (1)$$

where D is particle size in nanometer, ε is the strain component without dimensionless, k is a constant equal to 0.94, λ is wavelength of radiation (1.54056 Å° for Cu K α radiation), β_{hkl} is diffraction peak width at half-maximum intensity, and θ is diffraction angle. By plotting $\beta_{hkl} \cos \theta$ versus $4 \sin \theta$, we provides more of the crystal structure details, such as the slope and y-intercept of the fitted line represent strain and particle size parameter, respectively.

Equation S(2) To measure electrochemical capacitance, the potential was swept between 0.28 and 0.38 V versus Hg/HgO at ten different scan rates (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100), as shown in Figure S18. The measured capacitive currents are plotted as a function of scan rate and the linear slope is equivalent to twice of the C_{dl} . Ni(Fe)O_xH_y have been determined with an areal capacitance of $\sim 80 \mu\text{F cm}^{-2}$ in the charged state. The specific capacitances for Carbon Clothes, Ni LDH, Fe_{0.03}-Ni LDH, Fe_{0.03}W_{0.03}-Ni LDH and Fe_{0.03}W_{0.03}-Ni LDH^B are determined as 1.8, 1.9, 1.5, 1.7 and 2.9 mF cm⁻², respectively. ECSA is calculated as follows:

$$A_{ECSA} = \frac{C_{dl}^{sample}}{80\mu F^{NiO}} \quad (2)$$

Equation S(3) For temperature-dependent measurements, the kinetics of the OER are increased at elevated temperatures from 20°C to 60°C, reflecting the temperature dependence of the chemical rate constant, which is approximately proportional to $\exp(-\Delta H^*/kT)$. The Arrhenius equation is (3),

$$\frac{\partial(\log i_k)}{\partial(1/T)} = \frac{-\Delta H^*}{2.3R} \quad (\eta = 300mV)$$

where ΔH^* is the apparent enthalpy of activation (here after simply termed as the activation energy), i_k is the kinetic current at $\eta = 300$ mV, T is the temperature, and R is the universal gas constant.

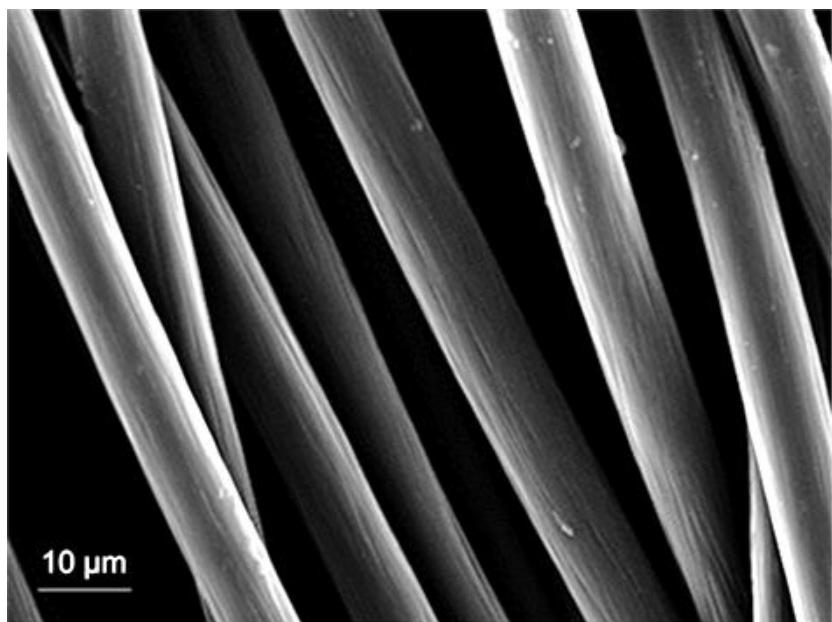


Fig. S1 SEM image of carbon fiber clothes

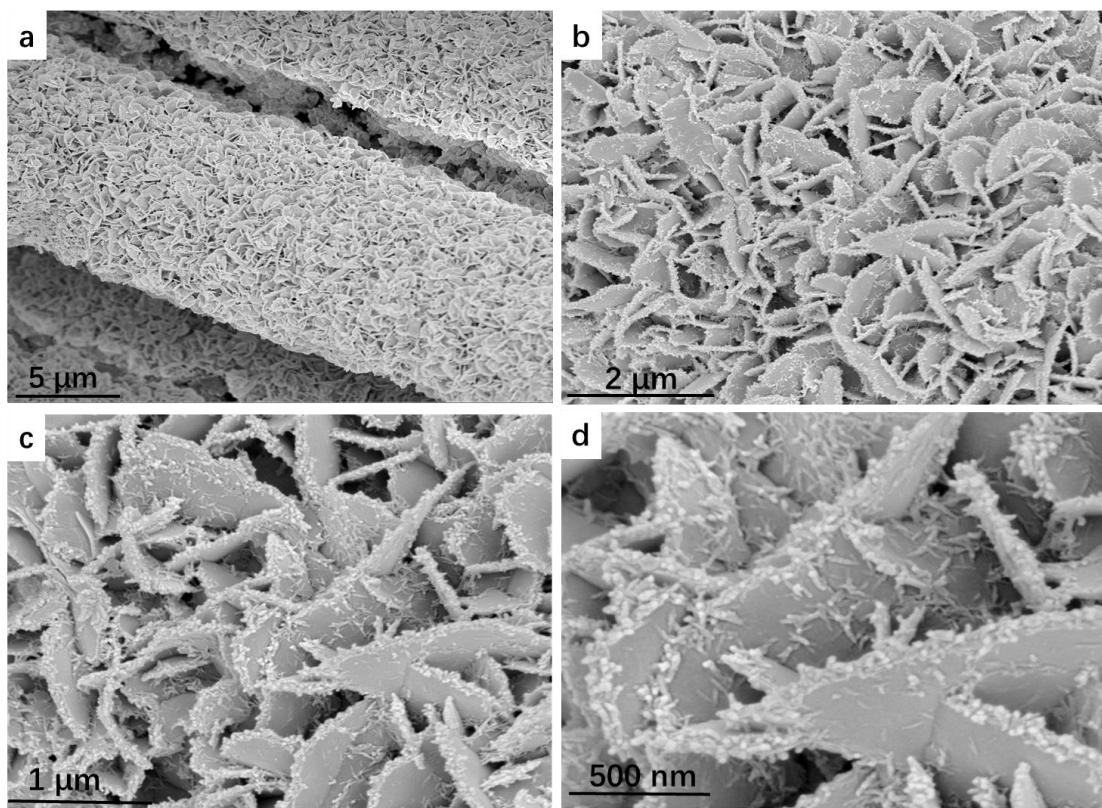


Fig. S2 SEM images of Fe_{0.03}W_{0.03}-Ni LDH samples

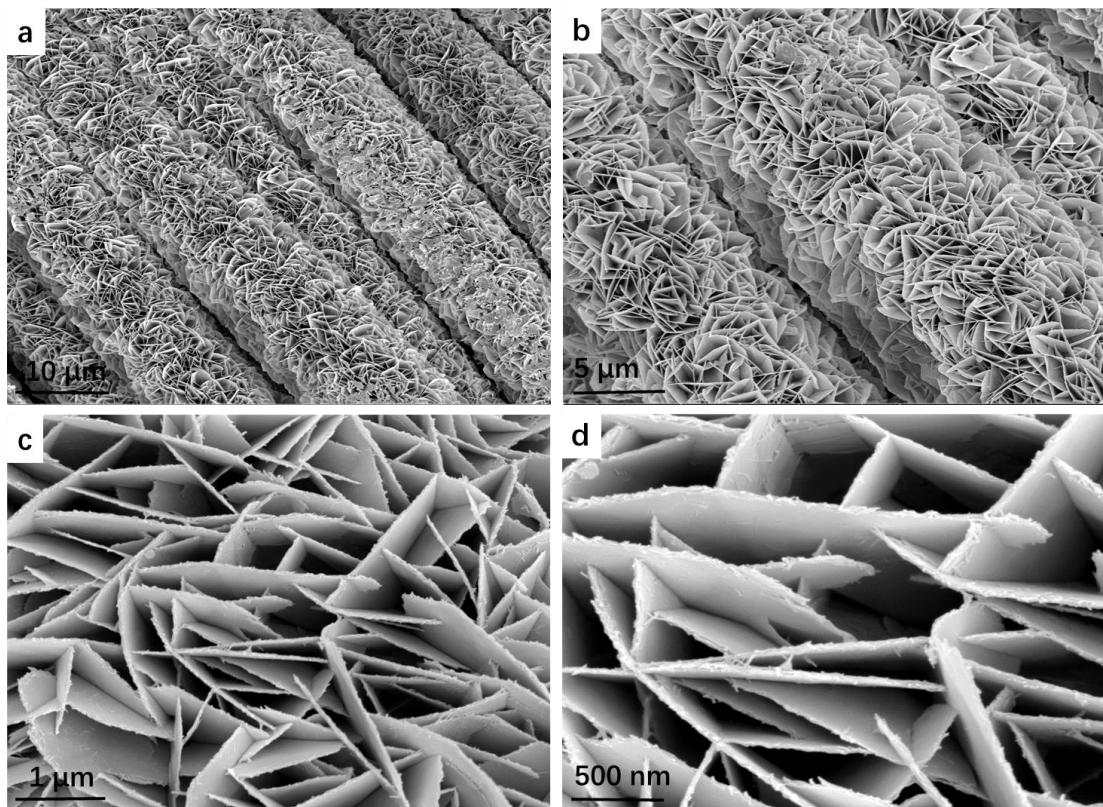


Fig. S3 SEM images of $\text{Fe}_{0.03}\text{-Ni}$ LDH samples.

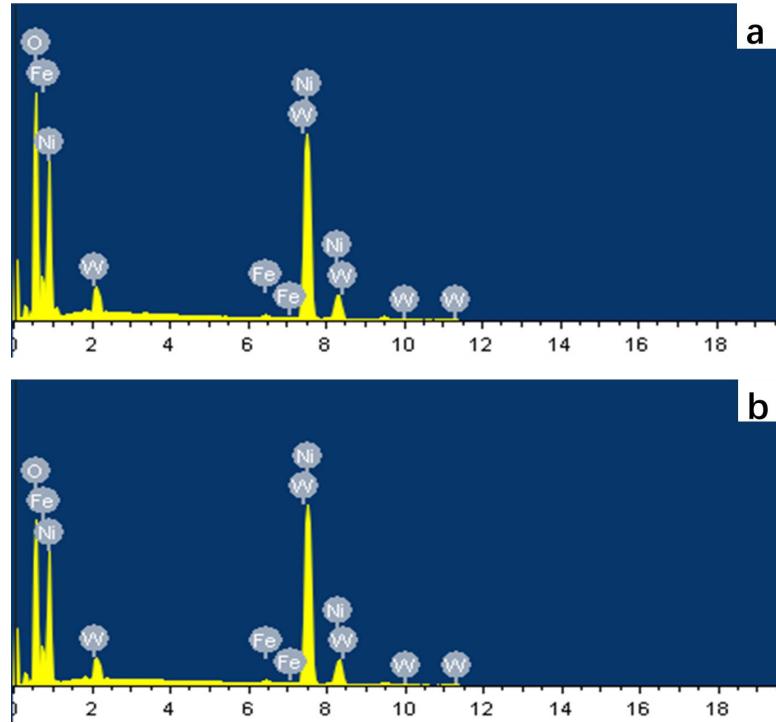


Fig. S4 EDX spectrum. a) $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni}$ LDH^B b) Post-OER $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni}$ LDH^B

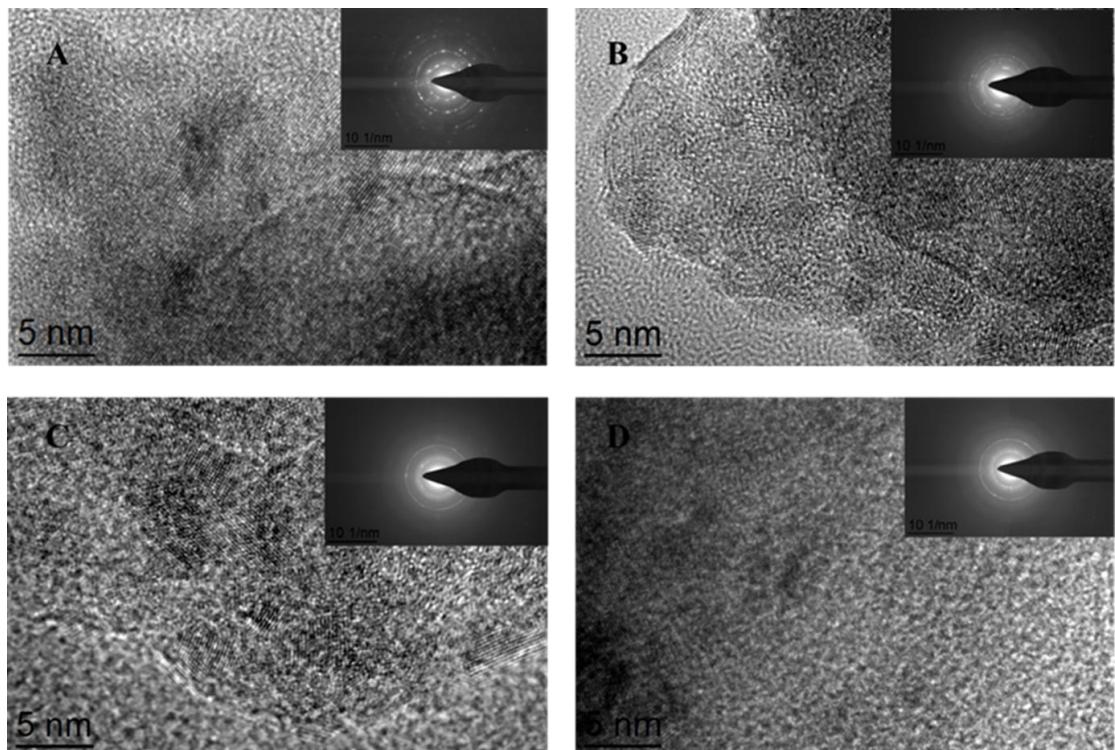


Fig. S5 (a-d) HR-TEM images of $\text{Fe}_{0.03}\text{Ni}$ LDH, $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni}$ LDH, $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni}$ LDH^B, post-OER $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni}$ LDH^B and corresponding SAED patterns (insert).

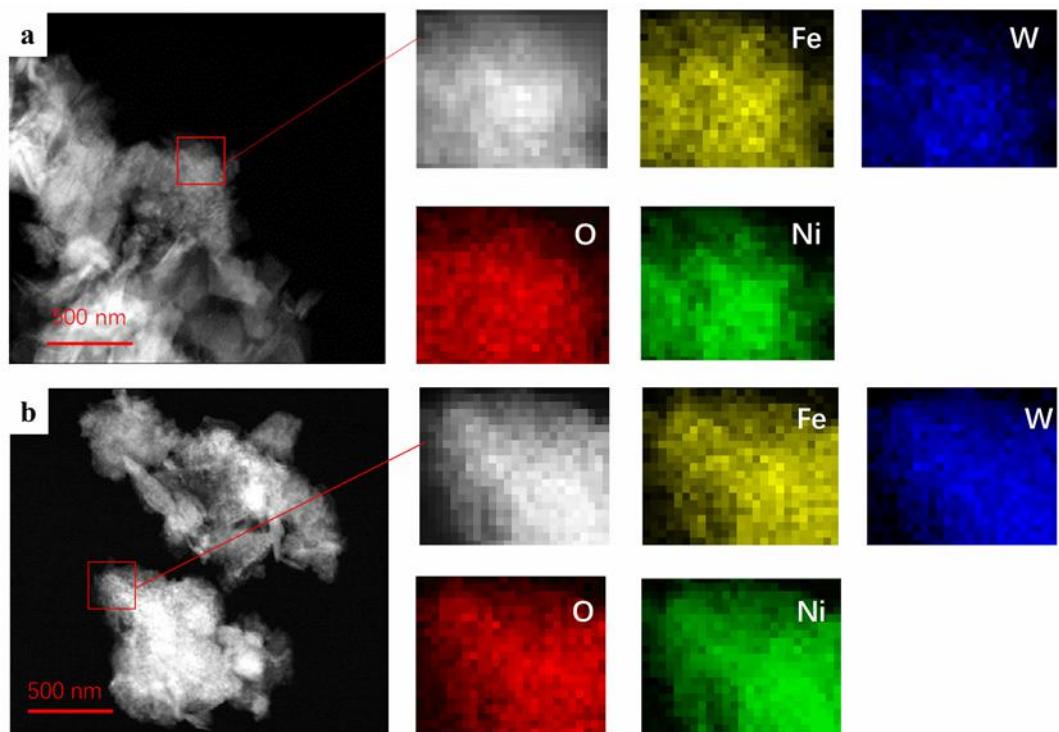


Fig. S6 Scanning transmission electron microscopy (STEM) images and the corresponding elemental mapping of Ni, Fe, W, and O. a) $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni}$ LDH; b) post-OER $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni}$ LDH^B.

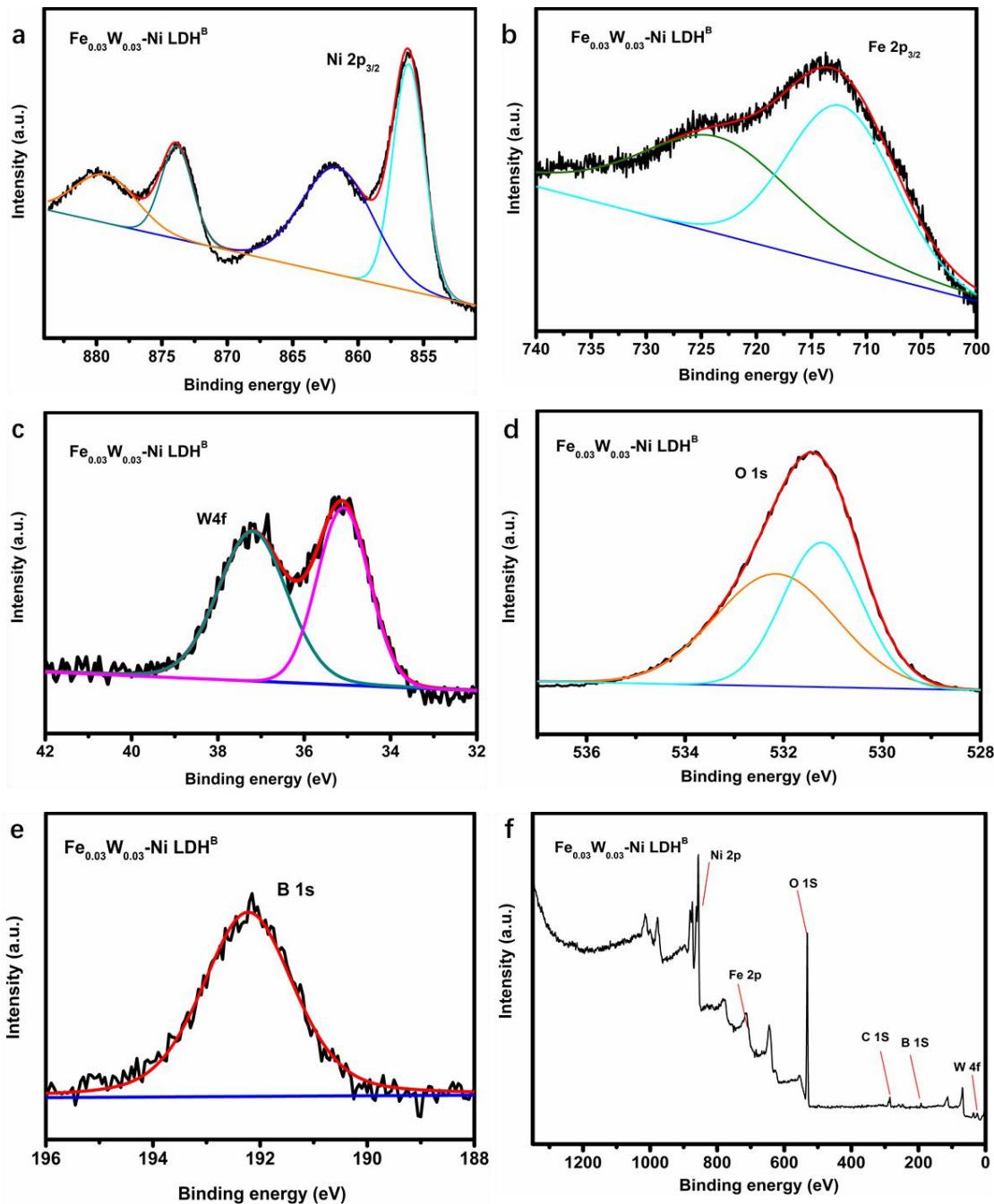


Fig. S7 a-e) XPS fine structures spectrum for $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$ in Ni 2p, Fe 2p, W 4f, O 1s and B 1s regions. f) XPS survey spectra of $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$.

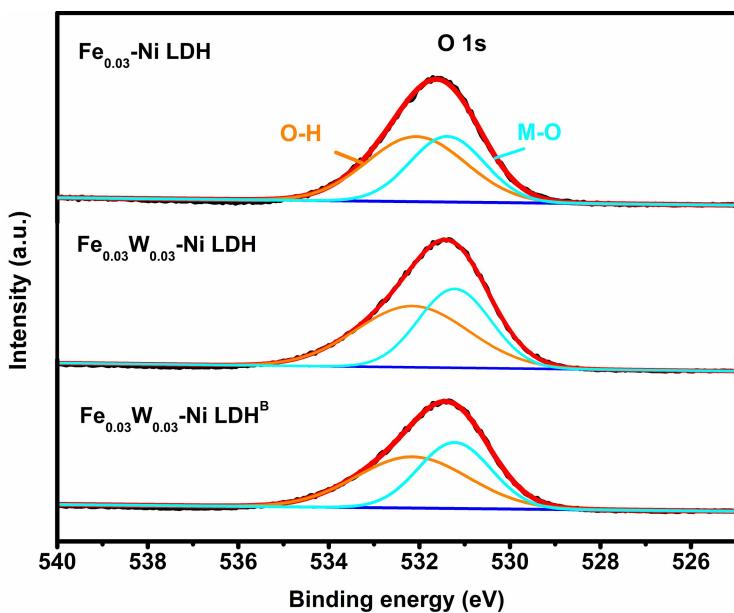


Fig. S8 XPS spectrum for $\text{Fe}_{0.03}\text{-Ni LDH}$, $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}$ and $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$ in O1s regions.

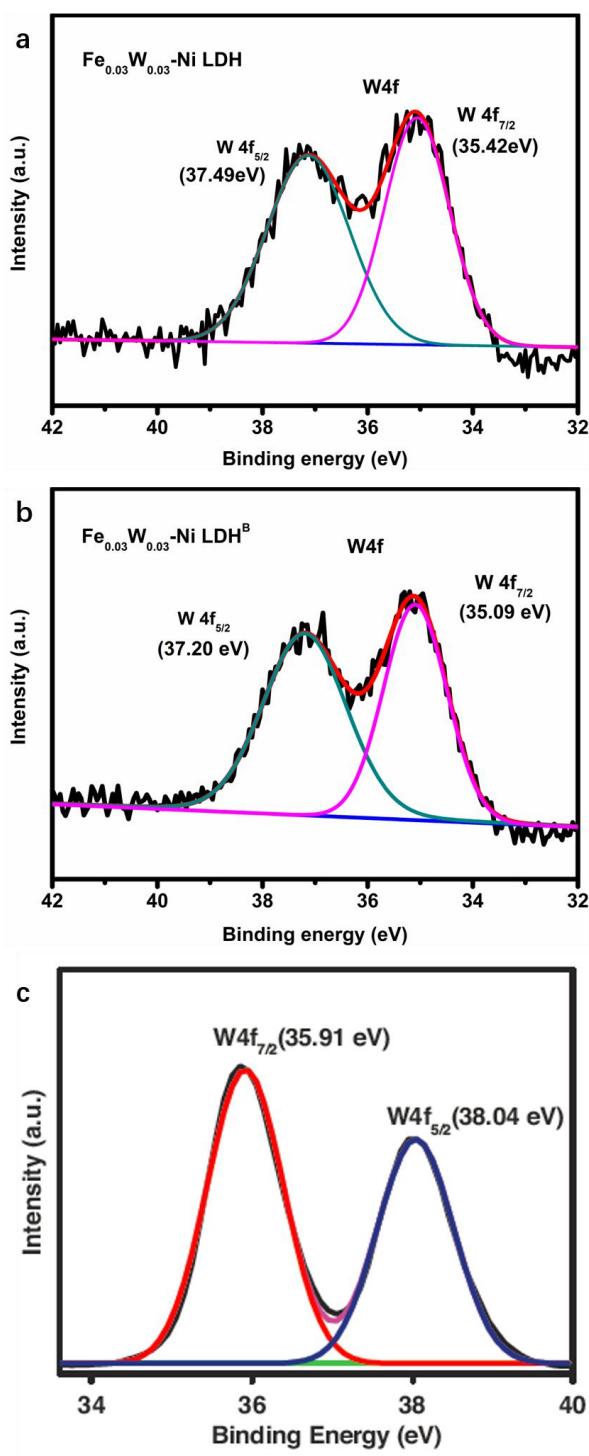


Fig. S9 XPS spectrum for a) $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}$, b) $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$ and c) $\text{WO}_3^{[38]}$ in W4f regions.

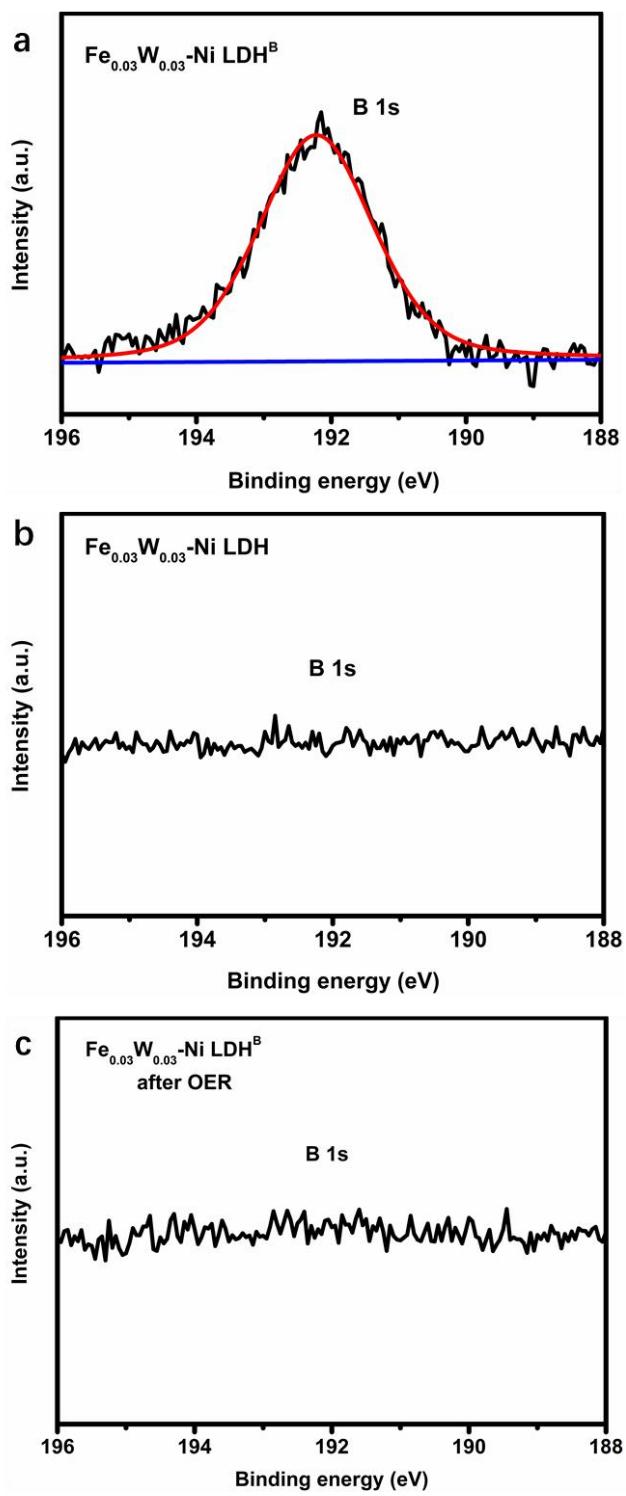


Fig. S10 XPS spectrum for a) $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}$, b) $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$ and c) $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$ after OER in B1s regions.

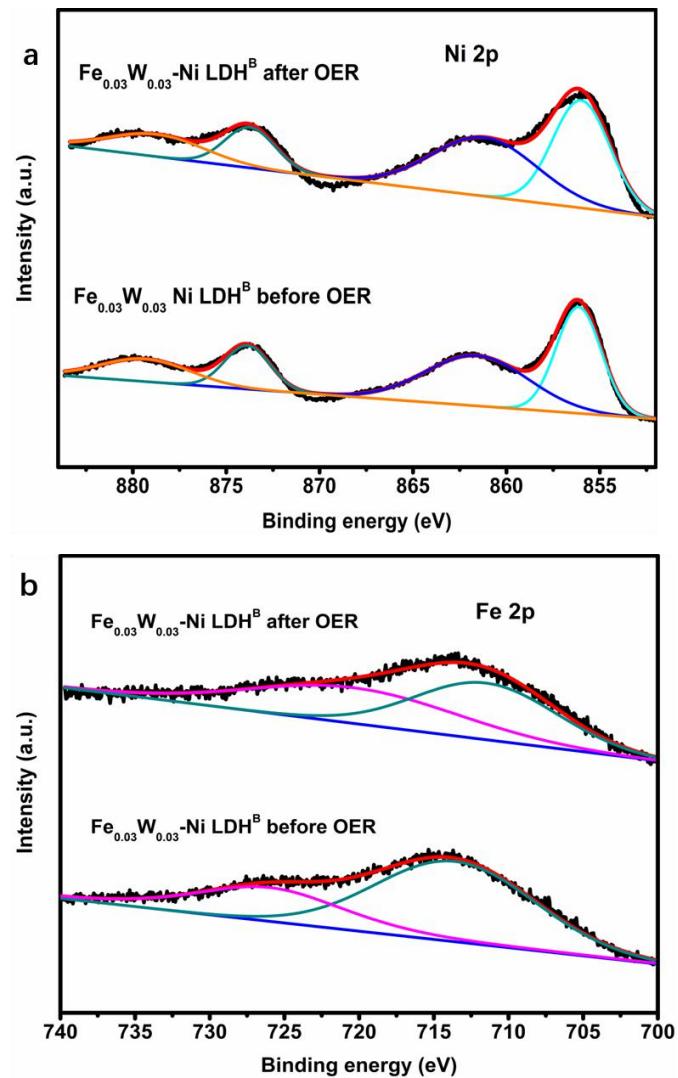


Fig. S11 XPS spectra for $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$ in a) Ni2p and b) Fe2p regions before and after oxygen evolution reaction.

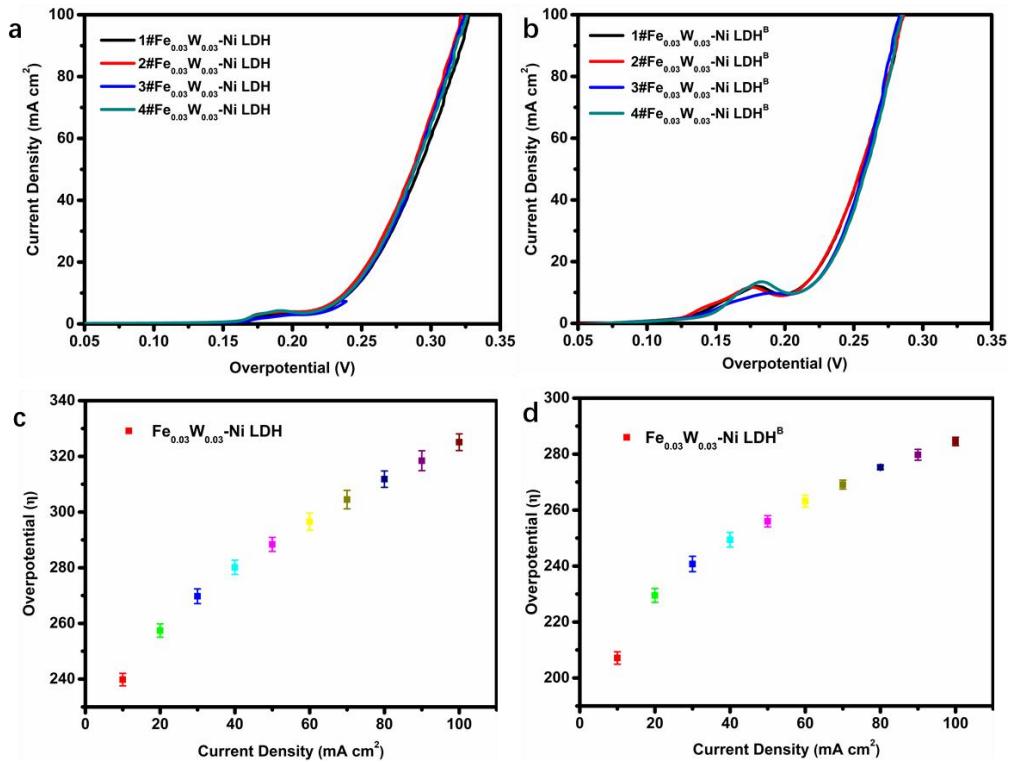


Fig. S12 Four independent OER polarization curves and scale bars of a,c) $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}$ and b,d) $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$ catalysts on carbon clothes.

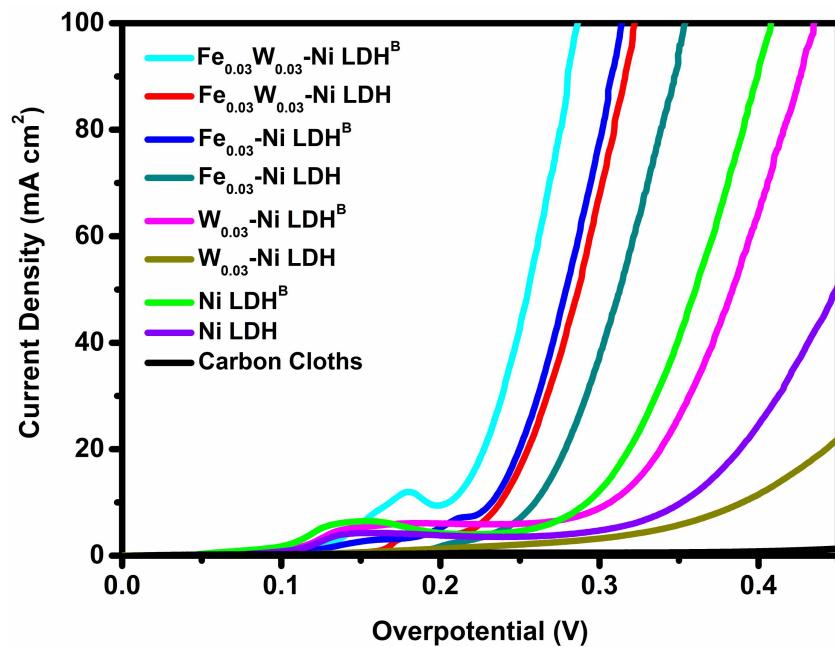


Fig. S13 LSV (Linear scan voltammetry) for more OER catalyst materials.

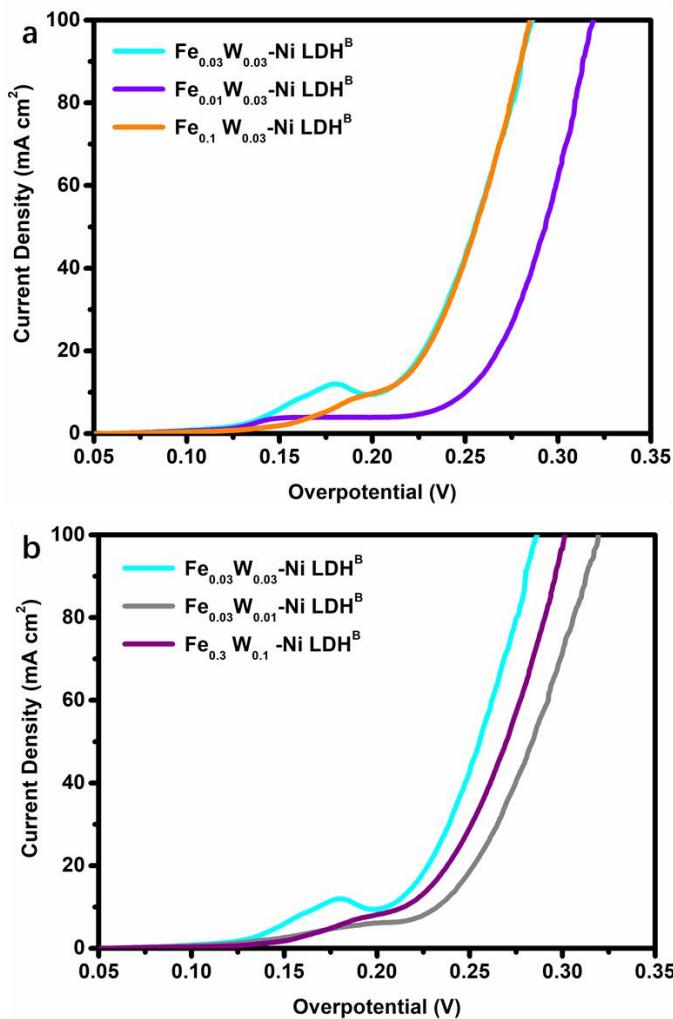


Fig. S14 a,b) LSV curves for different Fe,W atoms ratio of $\text{Fe}_x\text{W}_y\text{-Ni LDH}^{\text{B}}$ OER catalyst materials.

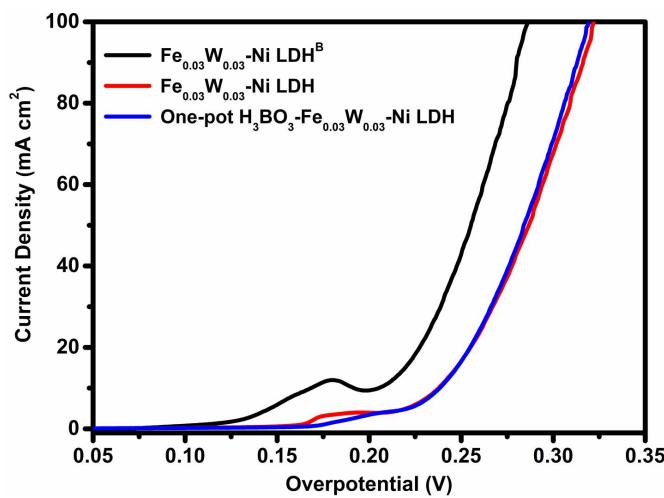


Fig. S15 LSV curves of samples doping with/without B element.

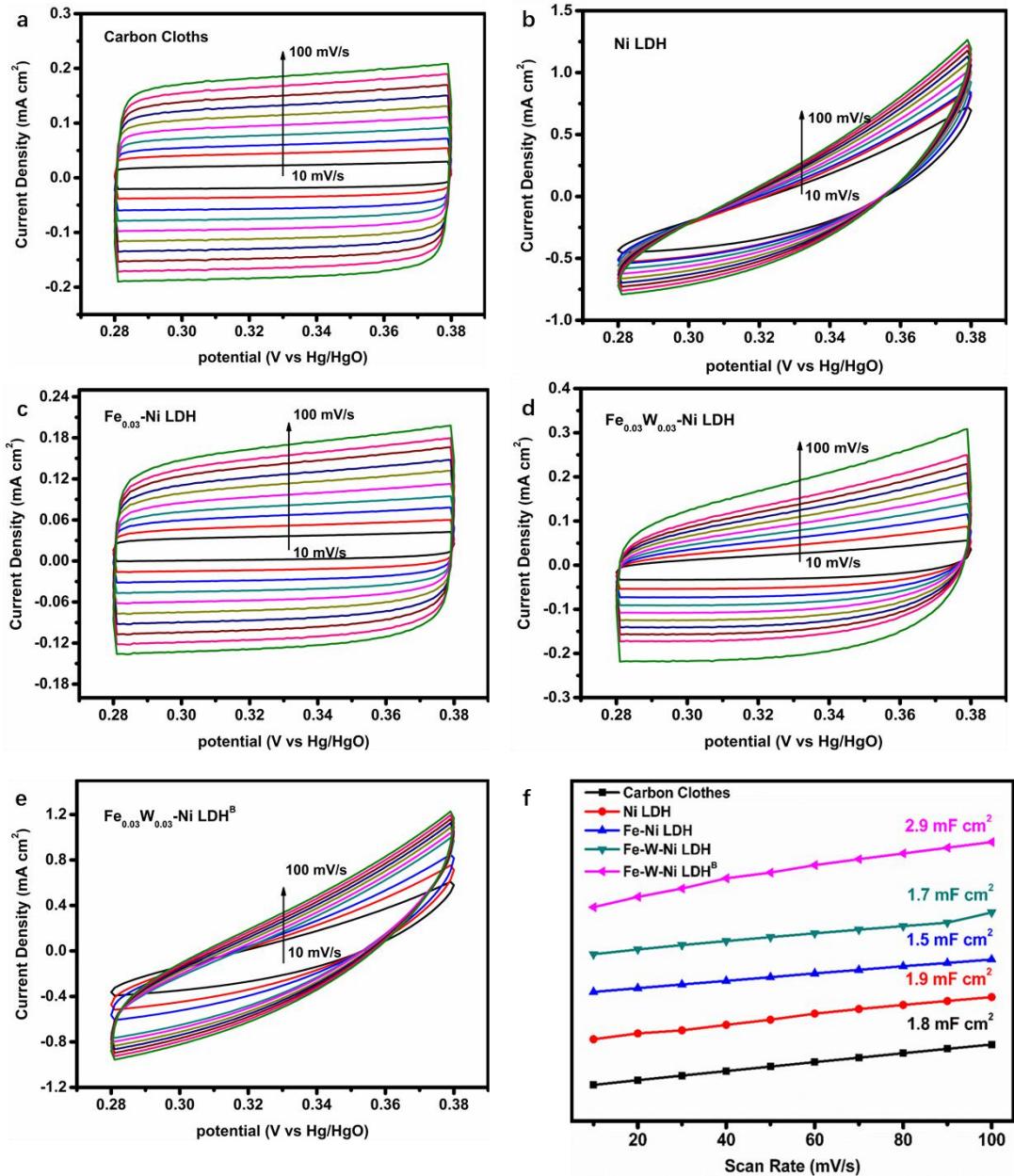


Fig. S16 a-e) Cyclic voltammograms of Carbon Clothes, Ni LDH, $\text{Fe}_{0.03}\text{-Ni LDH}$, $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}$ and $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^B$ at scan rates from 10 to 100 mV S^{-1} . f) Double layer capacitance values (Cdl) of Carbon Clothes, Ni LDH, $\text{Fe}_{0.03}\text{-Ni LDH}$, $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}$ and $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^B$.

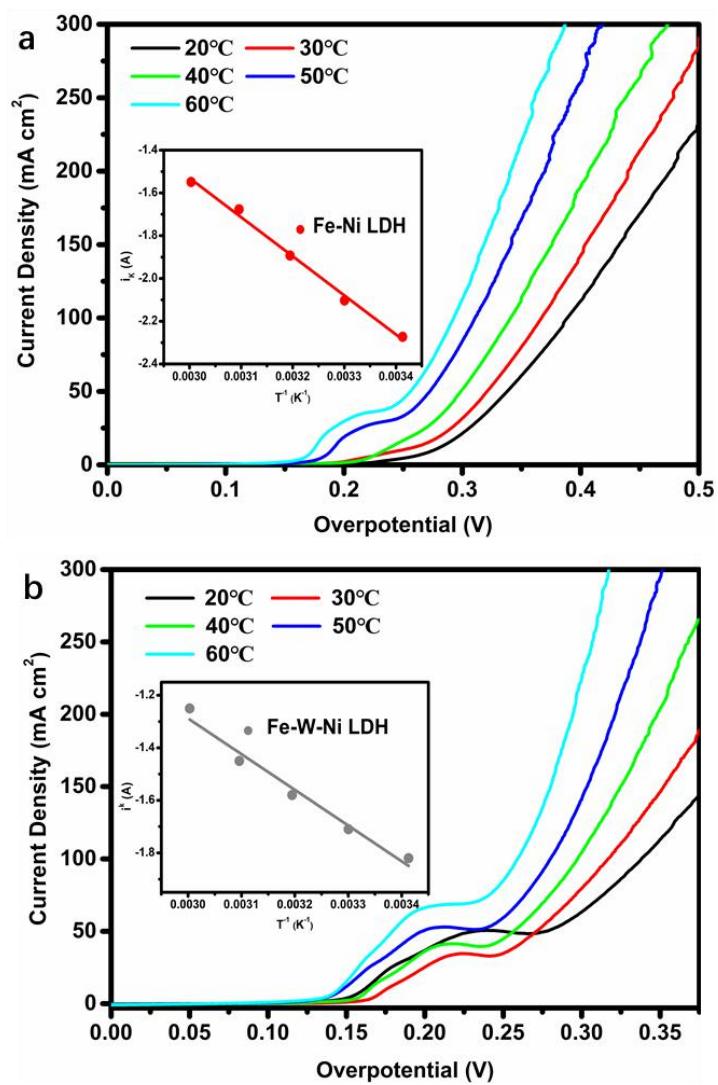


Fig. S17 The OER LSV curve of a) $\text{Fe}_{0.03}\text{-Ni LDH}$, b) $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}$ catalysts in 1 M KOH aqueous electrolyte loaded on carbon clothes with scan rate 5 mV s⁻¹ at 20°C, 30°C, 40°C, 50°C and 60°C, respectively.

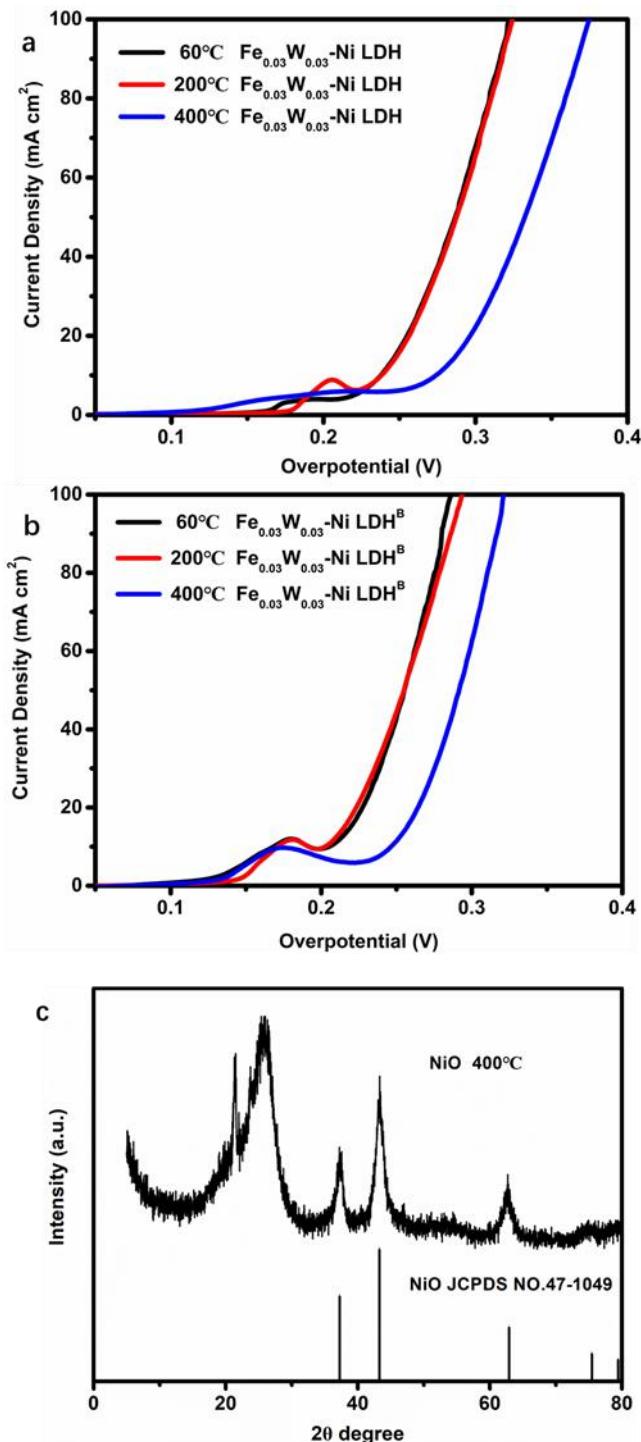


Fig. S18 a,b) LSV curves of $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}$ and $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$ with different annealed temperature. c) XRD pattern of sample after 400°C annealed.

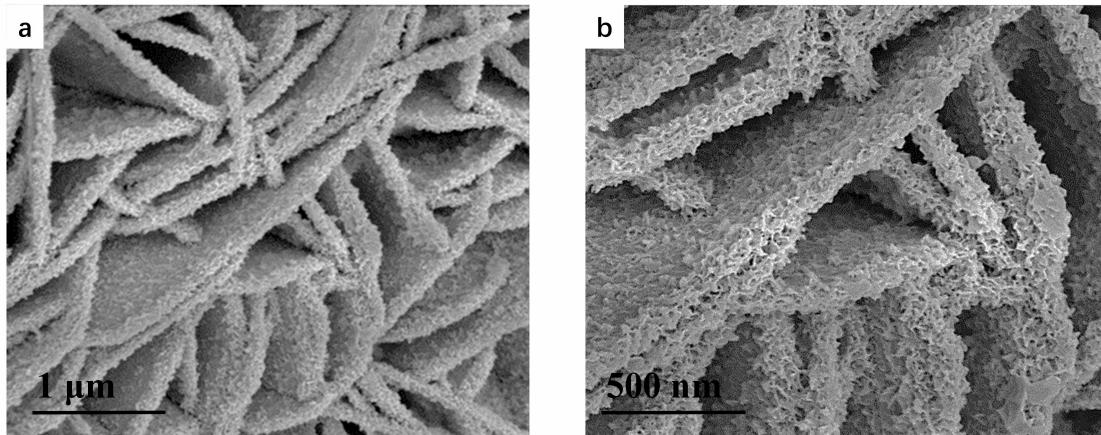


Fig. S19 a,b) SEM images of $\text{Fe}_{0.03}\text{-W}_{0.03}\text{-Ni LDH}^{\text{B}}$ samples after OER.

Table S1 ICP data of $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}$, $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$ and $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$ after OER

| materials | elements | Concentration (mg/L) | molar ratio (%) |
|--|----------|----------------------|-----------------|
| $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}$ | Fe | 3.572 | 3.97 |
| | W | 5.792 | 1.96 |
| | Ni | 88.85 | 94.07 |
| $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$ | Fe | 2.267 | 4.00 |
| | W | 4.364 | 2.34 |
| | Ni | 53.86 | 93.66 |
| | B | 4.769 | -- |
| $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$ after OER | Fe | 4.99 | 4.62 |
| | W | 9.19 | 2.59 |
| | Ni | 105.3 | 92.79 |
| | B | 1.362 | -- |

Table S2 Comparison of OER performance in 1.0 M KOH for $\text{Fe}_{0.03}\text{-W}_{0.03}\text{-Ni LDH}^{\text{B}}$ with other non-noble-metal electrocatalysts.

| Samples | η (mV) on carbon cloth | η (mV) on nickel foam | η (mV) on gold foam | References |
|---|-----------------------------|------------------------------|--------------------------|--|
| $\text{Fe}_{0.03}\text{W}_{0.03}\text{-Ni LDH}^{\text{B}}$ | 205 | 250(50 mA cm ⁻²) | — | This work |
| Gel-FeCoW | — | — | 191 | <i>Science</i> 2016 , <i>352</i> , 333. |
| CoFeW clusters | 205 | — | 192 | <i>J. Am. Chem. Soc.</i> 2019 , <i>141</i> , 232. |
| W-doped NiCoP | — | 330(50 mA cm ⁻²) | — | <i>J Mater Chem A</i> 2019 , <i>7</i> , 16859 |
| Ball-milling NiFe NP | 270(glassy carbon) | — | — | <i>Angew Chem Int Edit.</i> 2019 , <i>58</i> , 736. |
| Dry exfoliation NiFe NP | 276(glassy carbon) | — | — | <i>Angew Chem Int Edit.</i> 2017 , <i>56</i> , 5867. |
| $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2\text{ LDH}$ | 251 | — | — | <i>Adv Mater.</i> 2018 , <i>30</i> , 1802121. |
| NiCoP/NiFe LDH | — | 220 | — | <i>Adv. Funct. Mater.</i> 2018 , <i>28</i> , 1706847. |
| NaBH_4 soaked Fe-Co_xO_y | — | 204 | — | <i>Nano Energy</i> 2018 , <i>54</i> , 238. |