Supporting Information

Dual In Situ Laser Techniques Underpin the Role of Cations in Impacting Electro catalysts

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4. Supplementary References
1. Experimental Section

**Chemicals.** Terephthalic acid (TA, 98%), 16-mercaptobenzothiazole (MHDA, 90%), and CsOH (solution, 50 wt.% in H₂O, 99.9% trace) were purchased from Sigma-Aldrich. Nickel (II) chloride hexahydrate (NiCl₂·6H₂O, 99.3%), LiOH (99.995%), NaOH (99.99%), and KOH (99.98%) were obtained from Alfa Aesar. Trimethylamine (Et₃N) and absolute ethanol (99.9%) were purchased from Acros and Th. Geyer GmbH & Co. KG (Germany), respectively. Iron (III) chloride (FeCl₃, 98%) was purchased from abcr GmbH & Co. KG (Germany). All chemical reagents were used without further purification. Ultrapure water (18.2 MΩ cm) used in this work was prepared from a water purification system (Evoqua Ultra Clear 10 TWF 30 UV, Germany).

**Surface functionalization of gold electrodes.** Prior to the deposition of SURMOFs, the 5 MHz quartz crystal microbalance (QCM) gold substrates (Biolin Scientific, Inc.) were modified by immersing them in MHDA (20 μM) and acetic acid (5 vol.%) mixed ethanol solution for 12 h. Subsequently, the QCM gold substrates were washed carefully with ethanol three times.

**Deposition of Ni|Fe-[TA]-SURMOFs.** The deposition was carried out through a layer-by-layer (LBL) method in a home-made pump system. In particular, 0.25 mM NiCl₂·6H₂O and 0.25 mM FeCl₃ ethanol solutions were prepared as two kinds of metal ion sources, and the deprotonated organic linker solution (0.2 mM) was obtained by stirring TA (0.185 mmol), ethanol (1.02 L), distilled water (60 mL) and Et₃N (0.8 mL) for 24 h. For the LBL deposition, the pump system was stabilized at under 70 °C, and the surface-functionalized gold electrode was first immersed into the NiCl₂·6H₂O solution for 10 min, followed by an ethanol washing step for 2 min to remove unadsorbed species. Subsequently, the electrode was immersed into the deprotonated organic linker solution for 10 min to guarantee the generation of metal-organic bonds. Afterward, absolute ethanol was flushed through the system for 2 min to remove unreacted organic linkers. Four immersion processes represent one LBL deposition cycle. As the bottom layers in Ni|Fe-[TA]-SURMOFs, the Ni-[TA] was obtained after repeating the explained cycle 45 times. The NiCl₂·6H₂O solution was then replaced by the FeCl₃ solution in the subsequent 15 cycles to prepare the Fe-[TA] top-layer. Finally, the as-prepared heterostructured Ni|Fe-[TA]-SURMOFs electrode was rinsed carefully with absolute ethanol and dried at room temperature.

**Electrochemical measurements.** All electrochemical experiments were performed using a typical three-electrode setup in O₂-saturated 0.1 M solutions of alkali metal hydroxides. The as-prepared samples deposited on a commercial QCM electrode (diameter: 10 mm, geometric area: 0.785 cm²), a Pt mesh, and Hg/HgO (1 M NaOH, Bio-Logic, France) served as working, counter and reference electrodes, respectively. All the potentials were referenced to the reversible hydrogen electrode (RHE) scale. Before the electrochemical measurements, the SURMOF electrodes were immersed in the corresponding electrolyte for 3 min. Then cyclic voltammograms (CVs) were recorded at a scan rate of 20 mV s⁻¹ within the potential range of 1.14 and 1.54 V vs RHE for 40 cycles, using a Bio-Logic VSP-300 potentiostat. Afterward, the polarization curves were recorded with a lower scan rate of 5 mV s⁻¹ for 5 cycles. Note that all the OER polarization curves were automatically iR-corrected (95%).

**Electrochemical impedance spectroscopy (EIS) characterization.** The electrochemically active surface area (ECSA) was determined by the EIS method on a rotator (Pine Research Instrumentation). First, the heterostructured Ni|Fe-[TA]-SURMOFs were synthesized on a functionalized gold disk electrode (5 mm in diameter) using the LBL method. In the following, the as-prepared SURMOF electrode was transformed into the highly active catalysts by the alkaline immersion treatment and the CV cycling as mentioned in the above electrochemical measurement. To reduce the effect of "sample history", linear sweep voltammetry was performed at a slow scan rate of 0.5 mV s⁻¹ until the starting potential of the EIS measurement. Then, the EIS was carried out in a potential range of 1.30–1.61 V vs RHE with a 10 mV step. A frequency range from 30 kHz to 10 Hz and a 10 mV probing amplitude were used in this measurement.

**X-ray diffraction analysis.** Grazing incidence X-ray diffraction (GIXRD) patterns of all samples were investigated on an XPert PRO PANanalytical instrument (Ni-filtered Cu Kα radiation source) at a 2θ range of 5 to 35° with a slow-scanning step 0.125° per min.

**SEM measurements.** These samples were prepared by the same procedure but using Au-coated silicon plates (1.5 cm × 1.5 cm) instead of QCM electrodes as substrates. The morphologies of the SURMOFs and the derived catalysts were observed on an NVision40 FESEM (Carl Zeiss AG) machine with an accelerating voltage of 5 kV and a working distance of 3.5 mm.

**XPS measurements.** X-ray photoelectron spectroscopy (XPS) analysis was conducted on a SPECS setup (SPECS XR50 X-Ray source, anode: Al, 1487 eV, a SPECS PHOIBOS 150 hemispherical analyzer and SPECS spectrometer). The data were analyzed with the XPS Peak software to obtain the chemical constituents. The binding energies were corrected by referencing the C-C peak of the C 1s spectrum to 284.8 eV.
**SUPPORTING INFORMATION**

**In-situ Raman spectroscopy.** All the *in-situ* Raman experiments were performed on a Raman microscope (Renishaw inVia Reflex) with a 532 nm laser source. The electrochemical data were acquired in a homemade *in-situ* Raman cell with a quartz window and a typical three-electrode setup, using a potentiostat (Autolab PGSTAT302N). The collection of *in-situ* Raman spectra was carried out during the chronoamperometric measurements at selected biases. Each *in-situ* spectrum was recorded by accumulating three scans from 50 to 2000 cm$^{-1}$. To show the partial Raman peaks more clearly, some spectra within the range of 300 to 700 cm$^{-1}$ were fitted with a Gaussian function.

**Inductively coupled plasma atomic emission spectroscopy (ICP-OES).** The contents of Ni and Fe in the electrolytes (immersion treatment) and catalysts were determined by ICP-OES. The as-prepared SURMOF electrode was immersed in different electrolytes for 3 min, and then the obtained electrolytes (5 mL) were acidified by 5 mL 20 vol% ultrapure nitric acid (≥99.999%, Aldrich). In addition, after the electrochemical activation and OER test, the catalysts were dissolved in 10 mL 10 vol% ultrapure nitric acid for the ICP-OES measurement (700 Series ICP-OES by Agilent Technologies).

**Energy-dispersive X-ray spectrometry (EDS) analysis:** The elemental distributions in Ni|Fe-[TA]-SURMOFs were performed by using EDS (Bruker super-X EDS) in the SEM (ZEISS EVO).

**Density functional theory (DFT):** All the DFT calculations were performed using the Vienna Ab InitioSimulation Package (VASP) package. The generalized gradient approximation with the Perdew–Burke–Ernzerhof exchange-correlation functional (GGA-PBE) was used with a 400 eV cut-off energy to expand the electronic wave functions. In this study, the (0 0 1) surface was modeled by using a (1 × 2 × 1) supercell. The Monkhorst-Pack 5 × 5 × 1 K-point mesh was applied to the sample for the structural optimization and the electronic property calculations. The vacuum was separated by 20 Å to avoid interaction along the z direction. The force and energy convergence criterions were set to 0.01 eV Å$^{-1}$ and 10$^{-5}$ eV, respectively.

**Laser-induced current transient (LICT) experiments.** The LICT measurements were carried out using a Quanta-Ray INDI-Series pulsed Nd:YAG laser (Spectra Physics Lasers) and a custom-made three-electrode cell (as shown in Figure 4a). The laser with a 5-8 ns pulse width worked at a repetition rate of 10 Hz and a wavelength of 532 nm. Its beam diameter was ca. 9 mm. To avoid damaging the electrode, an attenuator (VACB-532-CONEX, Newport Corp) was used to control the energy density of pulses at ca.12.5 mJ cm$^{-2}$. The SURMOF-coated AT-cut Au quartz crystal chip (Stanford Research Systems) was installed in a PTFE holder and used as the working electrode, while a Pt wire and Hg/HgO (1.0 M NaOH) served as the counter and reference electrodes, respectively. Prior to the LICT measurement, the SURMOF electrodes were activated in another homemade PTFE cell by both CV cycling and OER testing. In particular, the SURMOFs were immersed in the corresponding electrolyte for 3 min, and then a CV was recorded at a scan rate of 20 mV s$^{-1}$ within a potential range of 1.14 and 1.54 V vs RHE for 40 cycles. Afterward, OER tests were conducted at a scan rate of 5 mV s$^{-1}$ within a larger potential range of 1.20-1.70 V vs RHE for cycles. This activation could result in the structural transformation and the linker leaching from the pristine SURMOFs. In the LICT measurements, the working electrode was placed facing the quartz window (ø = 30 mm) of the cell to facilitate the vertical laser irradiation, and fresh electrolytes were used. The investigated potential range was between 0.81 and 1.21 V vs RHE with potential steps of 20 mV. All transient current curves were recorded by the chronoamperometry method with an “auto” setting of the current range and a record of every 0.0004 s.
2. Supplementary Figures

Figure S1. Potential calibration of the Hg/HgO (1 M NaOH) reference electrode. The calibration experiment was carried out in high purity H₂ saturated 0.1 M NaOH (pH = 13.1) electrolyte. A Pt wire and a Pt mesh were used as the working electrode and the counter electrode, respectively. The Pt wire was placed close to the reference electrode. The CV test was performed at a scan rate of 5 mV s⁻¹ within a potential region of -0.75 to -1.05 V vs Hg/HgO. Taking the 0 mA current, two voltages intersecting the x-axis are -0.902 and -0.912 V, respectively. The corresponding average potential (-0.907 V) represents the thermodynamic potential of the hydrogen evolution reaction. Our result shows that $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.134 \text{ V} + 0.059^*\text{pH}$. 
**Figure S2.** Morphological characterization. SEM images of NiFe-[TA]-SURMOFs (a) and cross-section characterization with angle of 45˚ (b). (c) The EDS elemental maps of NiFe-[TA]-SURMOFs. (d) SEM images of Ni-[TA]-SURMOFs thin film (45 layers) growth on the gold QCM electrode.
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High-resolution XPS spectra of C 1s reveal the existence of organic linkers in both pristine SURMOFs and the derived catalysts as the surface species display C=C, C-C, C=O, and O-C=O bonds (Figure S5a). As shown in Figure S5b, the O 1s spectra can be deconvoluted into four peaks, corresponding to the O=C-O group, C-O bonds, Ni(Fe)-oxygen bonds, and Ni(Fe)-hydroxyl species, respectively. These results further confirm the existence of residual organic linkers in the derived catalysts. Their relative content is, however, much less than in the as-prepared SURMOFs, suggesting that most organic linkers leached out during the transformation process. In contrast, the XPS peak areas of Ni(Fe)-hydroxyl species increased after the electrochemical cycling in the alkaline electrolytes (Table S4). This can be ascribed to the transformation of SURMOFs into NiFe(oxy)hydroxide species. The Ni 2p spectrum of the SURMOFs (Figure S5d) possesses two main peaks at ca. 856.56 and 874.47 eV, corresponding to Ni 2p\textsubscript{3/2} and Ni 2p\textsubscript{1/2}, in line with the presence of Ni\textsuperscript{2+} in the pristine SURMOFs. Note that distinct peaks can be found at a higher binding energy of ca.
857 eV and ca. 873 eV in the derived catalysts, ascribed to Ni$^{3+}$ oxidation state species. This supports the assertion that the SURMOFs were converted into NiFe(oxy)hydroxides during the electrochemical treatment in the alkaline aqueous electrolytes.
Figure S6. Voltammetric characterization. Cyclic voltammetry (CV) curves of NiFe-[TA]-SURMOF electrodes with a scan rate of 20 mV s\(^{-1}\) for 40 cycles in different electrolytes.
Figure S7. Mass detection. Comparison of the mass loading of Ni|Fe-[TA]-SURMOFs and NiFe-[TA]-Catalyst electrodes before and after OER measurement in different electrolytes.
Figure S8. Electrocatalytic performance. (a) Geometric activity curves and (b) Tafel plots of Ni[Fe-[TA]-Catalyst in O\textsubscript{2}-saturated 0.1 M LiOH, 0.1 M NaOH, 0.1 M KOH, and 0.1 M CsOH electrolytes. (c) The overpotentials of all samples at a current density of 10 mA cm\textsuperscript{-2} from four independent experiments.

The geometric area activities in different electrolytes have been provided in Figure S8, which present a similar trend as the mass activity. This result further discloses the enhancement effect of cations on the electrocatalytic OER activity of the SURMOF derivatives. In addition, the comparison of geometric area activity for recently reported advanced OER catalysts is provided in Table S2. The SURMOF-derived catalyst of this work shows an outstanding OER activity with an overpotential of 308.6 mV at 10 mA cm\textsuperscript{-2} in 0.1 M CsOH, compared with the MOFs, noble metals, and LDH catalysts in Table S2. Note that some catalysts supported on nickel foam or carbon cloth exhibit remarkable OER performance, but in these cases the currents divided by the geometric area of the electrode cannot accurately represent the real area activity, since nickel foam and carbon cloth substrates possess abundant porous structures and large surface areas, which are significantly higher than the geometric area of the electrode.\cite{7} Therefore, their activities may be overestimated. In addition, it is worth noting that our SURMOF derived catalyst achieved a distinguished performance at low catalyst loading.

To evaluate the intrinsic activity, the electrochemical active surface area (ECSA) of the catalysts in different electrolytes was determined by an electrochemical impedance spectroscopy (EIS) characterization.\cite{8,9,10} In detail, the NiFe-[TA]-SURMOFs were synthesized on a modified gold disk (5 mm in diameter) by the same LBL method. After the immersion and electrochemical activation processes in different electrolytes, EIS was conducted with a 10 mV potential step between 1.30 and 1.61 V vs RHE. The frequency range is from 200 kHz to 10 Hz and the probing amplitude is 10 mV. All EIS data were analyzed with the Armstrong-Henderson equivalent electric circuit (EEC) model on the EIS Data Analysis 1.3 software. An example of the impedance data fitting is shown in Figure S9a and S9b. As expounded in our previous work\cite{10}, the adsorption capacitance (C\textsubscript{a}) of catalytically active species can be used to accurately determine the ECSA based on the equation (ECSA = C\textsubscript{a}/C\textsubscript{a}'), where the specific adsorption capacitance C\textsubscript{a} for NiFe hydroxide is around 430 µF cm\textsuperscript{-2}. All polarization curves were normalized to the ECSA as shown in Figure S9c. Interestingly, NiFe-[TA]-Catalysts in various electrolytes exhibit a close C\textsubscript{a} value. In the polarization curves normalized by ECSA, the catalyst in presence of Cs\textsuperscript{+} shows the highest activity. The former indicates the active sites of all catalysts derived in different electrolytes exhibit similar intrinsic catalytic activity, therefore the performance discrepancy can be attributed to the effect of cations.
Figure S9. Determination of the intrinsic activity. (a) EIS data (triangle) of the NiFe-[TA]-Catalyst recorded in 0.1 M CsOH at the potential of 1.56 V vs RHE. The fitted line was obtained according to the equivalent electric circuit (EEC) model in the inset. (b) Adsorption capacitances as a function of applied potentials (1.30-1.61 V). (c) Adsorption capacitances of Ni[Fe-[TA]-Catalyst obtained by the EIS measurement in the O₂-saturated 0.1 M MOH electrolytes. The EIS characterization was conducted on a rotator (Pine Research Instrumentation) and a gold disk electrode (0.196 cm²) with a 10 mV steps and an applied potential range of 1.30-1.61 V. For more details on the measurement and analysis, please refer to the experimental section. (d) Polarization curves of Catalysts normalized by ECSA.
**Figure S10.** Electrocatalytic performance. (a) The mass loading of the pristine SURMOFs and derived Catalyst after the OER test recorded by the QCM electrode, (b) Polarization curves and (c) Tafel plots of Ni[Fe-[TA]-Catalyst in 0.1 M O₂-saturated RbOH with a scan rate of 5 mV s⁻¹. (d) The current densities obtained with the Ni[Fe-[TA]-Catalyst at an applied potential of 1.53 V vs RHE in 0.1 M MOH electrolytes. All error bars were gained through three independent experiments.

**Figure S11.** In-situ Raman spectroscopy. (a) Potential-dependent Raman spectra of the Ni[Fe-[TA]-Catalyst recorded in 0.1 M RbOH electrolyte. (b) The Gaussian fitting of the Raman spectrum measured at 1.70 V vs RHE within the wavenumber range of 300 to 700 cm⁻¹. (c) Correlation of the electrocatalytic activities acquired at 1.70 V vs RHE.
Figure S12. LICT measurement. (a) 3D current transient curves recorded by the LICT measurement in Ar-saturated 0.1 M RbOH. (b) The corresponding 2D values of the current transient spikes maxima (iXmax) as a function of the applied potentials. (c) Dependence of the electrocatalytic activities at 1.53 V vs RHE on the PME for Ni|Fe-[TA]-Catalyst electrode in different electrolytes.

In order to obtain better correlation for the OER enhancement effect of the alkali metal cations, the activity and the properties of the catalyst obtained in RbOH were systematically investigated. It’s worth noting that the oxygen evolution activity in RbOH and the hydration energy of Rb⁺ (~296 kJ/mol) do not follow the trend as moving down the alkali metal group from Li to Cs. The performance discrepancy can be observed in Figure S10, where the Ni|Fe-[TA]-Catalyst shows a general mass activity of ~0.56 kA g⁻¹ at 1.53 V vs RHE in RbOH, which is between the activities obtained in LiOH and NaOH. This inconsistent activity trend for Rb⁺ electrolyte indicates the difference of interaction mechanism in comparison to other alkali metal cations. Furthermore, as shown in Figures S11 an S12, in-situ Raman spectra and LICT data in RbOH reveal the correlations between the catalytic activity with the Raman shift and PME values, even though the Rb⁺ results in a degraded linear relationship in the alkali metal group. Thus, we merely mentioned the investigation of Rb⁺ effect on the properties of SURMOF-derived catalyst here.
Figure S13. Ex-situ Raman spectroscopy. Raman spectra collected during the 3-min immersion in 0.1 M CsOH for Ni|Fe-[TA]-SURMOFs electrode within a wavenumber region of 200-4000 cm⁻¹. CsOH immersion treatment was conducted such that the Ni|Fe-[TA]-SURMOF electrode was directly immersed in 0.1 M CsOH solution for 15, 30, 60, 120, and 180 s, respectively. After each immersion process, the electrode was washed with deionized water for three times and dried with argon flow.
Figure S14. In-situ Raman spectroscopy. In-situ Raman spectra of the Ni|Fe-[TA]-Catalyst collected in different electrolytes within the potential range of 1.20-1.70 V vs RHE.
Figure S15. Raman spectra of active OO$^-$ structure. *In-situ* Raman spectra collected over the Ni|Fe-[TA]-Catalyst and recorded within the potential range of 1.20-1.70 V vs RHE in different electrolytes. The frequency regions of the Raman spectra (800-1200 cm$^{-1}$) show the active structure OO$^-$ in NIOOH.
**Figure S16.** Stability tests on the Ni|Fe-[TA]-Catalyst recorded at current density of 10 mA cm$^{-2}$ in 0.1 M O$_2$-saturated MOH. All catalysts were derived from the SURMOFs, which were grown on the gold disk (0.196 cm$^2$).
**Figure S17.** Density functional theory calculations. (a, b) Structure models of the NiFe(OOH) electrocatalyst and the possible reactive sites at the O vacancy. The color palette for the chemical representation is as follows: green, Ni; wheat, Fe; blue, O; aqua, H; purple, cations; red, activated oxygen in reaction intermediates. (c) The oxygen evolution activities at 1.53 V vs RHE plotted as a function of the OH adsorption energies in presence of various cations. The OH species are adsorbed to form the reaction intermediate Ni(Fe)OOH.
Figure S18. 3D current transient curves recorded by the LICT measurement in Ar-saturated 0.1 M LiOH, NaOH, and KOH electrolytes. The potential range was performed from 0.81 to 1.21 V vs RHE.
3. Supplementary Tables

Table S1. Comparison of the electrocatalytic performance based on mass activity for recently reported OER catalysts.

| Catalyst                        | Current density (A·g⁻¹) at overpotential of 300 mV | Electrolyte (pH) | Ref.                                           |
|--------------------------------|---------------------------------------------------|------------------|------------------------------------------------|
| NiFe-[TA]-Catalyst             | ~360                                              | 0.1 M LiOH (12.9) | This work                                      |
|                                | ~602                                              | 0.1 M NaOH (13.1) |                                                |
|                                | ~701                                              | 0.1 M KOH (13.2)  |                                                |
|                                | ~802                                              | 0.1 M CsOH (13.3)|                                                |
| NiFe-MOF                       | 547.8                                             | 1.0 M KOH         | [11] _Adv. Funct. Mater._ 2021, 31, 2102066.    |
| FeₓCoᵧ-ONSSs                   | 54.9 at 350 mV                                    | 0.1 M KOH         | [12] _Adv. Mater._ 2017, 29, 1606793.          |
| MIL-53(FeNi)/NF                | 76.07 at 252 mV                                   | 1.0 M KOH         | [13] _Adv. Energy Mater._ 2018, 8, 1800584.    |
| NiCo-UMOFNs                    | 50 at 250 mV                                      | 1.0 M KOH         | [14] _Nat. Energy_ 2016, 1, 16184.             |
| Co₀.7Fe₀.3CB                   | 643.4 at 320 mV                                   | 1.0 M KOH         | [15] _Adv. Funct. Mater._ 2020, 30, 1909889.   |
| NiFe-LDH@NiCu                  | 429.1                                             | 1.0 M KOH         | [16] _Adv. Mater._ 2019, 31, 1806769.          |
| NiFe LDH nanomesh              | 257.8                                             | 1.0 M KOH         | [17] _Nano Energy_ 2018, 53, 74-82.            |
| Ni₀.8Fe₀.2OₓHᵧ                 | 140 ± 30                                          | 1.0 M KOH         | [18] _Chem. Mater._ 2017, 29, 120-140.        |
| Ni₅₀Fe₅₀-DAT                   | ~1200                                            | 1.0 M NaOH        | [19] _ACS Catal._ 2016, 6, 1159-1164.          |
| δ-FeOOH NSs/NF                 | 267                                               | 1.0 M KOH         | [20] _Adv. Mater._ 2018, 30, 1803144.          |
| CoMn LDH                       | 159                                               | 1.0 M KOH         | [21] _J. Am. Chem. Soc._ 2014, 136, 16481-16484. |
| P—Ni₀.75Fe₀.25Se₂              | 328.19 at 500 mV                                  | 1.0 M KOH         | [22] _Adv. Sci._, 2021, 8, 2101775.            |
| NiSe₂                          | 88.7                                              | 1.0 M KOH         | [23] _Electrochim. Acta_ 2019, 295, 92-98.     |
| 50Ni50Co-SURMOFD 10 cycles     | 2530                                              | 0.1 M KOH         | [24] _J. Am. Chem. Soc._ 2019, 141, 5926-5933. |
| NiFe-BTC-GNPs                  | 905                                               | 1.0 M KOH         | [25] _Energy Environ. Sci._ 2020, 13, 3447-3458. |

[11] _Adv. Funct. Mater._ 2021, 31, 2102066.
[12] _Adv. Mater._ 2017, 29, 1606793.
[13] _Adv. Energy Mater._ 2018, 8, 1800584.
[14] _Nat. Energy_ 2016, 1, 16184.
[15] _Adv. Funct. Mater._ 2020, 30, 1909889.
[16] _Adv. Mater._ 2019, 31, 1806769.
[17] _Nano Energy_ 2018, 53, 74-82.
[18] _Chem. Mater._ 2017, 29, 120-140.
[19] _ACS Catal._ 2016, 6, 1159-1164.
[20] _Adv. Mater._ 2018, 30, 1803144.
[21] _J. Am. Chem. Soc._ 2014, 136, 16481-16484.
[22] _Adv. Sci._, 2021, 8, 2101775.
[23] _Electrochim. Acta_ 2019, 295, 92-98.
[24] _J. Am. Chem. Soc._ 2019, 141, 5926-5933.
[25] _Energy Environ. Sci._ 2020, 13, 3447-3458.
| Material                          | Current Density (A g_{Ru}^{-1}) | Current Density (A g_{metal}^{-1}) | pH          | Reference                                               |
|----------------------------------|---------------------------------|-----------------------------------|-------------|---------------------------------------------------------|
| CaCu_{3}Ru_{4}O_{12}             | 1942                            |                                   | 0.5 M H_{2}SO_{4} | [26] Nat. Commun. 2019, 10, 3809.                      |
| RuO_{2} NSs                      | 520                             |                                   | 0.5 M H_{2}SO_{4} | [27] Energy Environ. Sci. 2020, 13, 5143-5151.         |
| Rh_{22}Ir_{78}/VXC               | 1020                            |                                   | 0.5 M H_{2}SO_{4} | [28] ACS Nano 2019, 13, 13225-13234.                   |
| RuO_{2} particle                 | 600                             |                                   | 0.05 M H_{2}SO_{4} | [29] Chem. Sci. 2015, 6, 190-196.                      |
| Co-IrCu ONC/C                    | 640                             |                                   | 0.1 M HClO_{4}  | [30] Adv. Funct. Mater. 2017, 27, 1604688.             |
| Ir-network                       | 817                             |                                   | 0.1 M HClO_{4}  | [31] J. Mater. Chem. A 2020, 8, 1066-1071.            |
| a-PN-IN frame/C                  | 644                             |                                   | 0.1 M HClO_{4}  | [32] Adv. Funct. Mater. 2020, 30, 2003935.            |
| IrO_{x}/9R-BaIrO_{3}             | 168                             |                                   | 0.5 M H_{2}SO_{4} | [33] J. Am. Chem. Soc. 2021, 143, 18001-18009.       |
Table S2. Comparison of the electrocatalytic performance based on area activity for recently reported OER catalysts.

| Catalyst | Overpotential [mV] at 10 mA cm$^{-2}$ | Substrate | Mass loading [mg cm$^{-2}$] | Ref. |
|----------|-------------------------------------|-----------|-----------------------------|------|
| Co$_3$HITP$_2$ | 360 | glass carbon | 0.27 | [34] Angew. Chem. Int. Ed. 2020, 59, 286-294. |
| Mn/Fe-HIB-MOF | 280 | glass carbon | 0.15 | [35] Energy Environ. Sci. 2019, 12, 727-738. |
| Co MOF/CC | 346 | carbon cloth | 0.24 | [36] Small 2021, 2105150 |
| NiFe LDH | ~350 | glass carbon | 0.10 | [37] Angew. Chem. Int. Ed. 2021, 60, 14446-14457. |
| Ni MOF | 346 | carbon paper | 0.48 | [38] ChemElectroChem 2018, 5, 2795. |
| Co$_3$O$_4$/CoMoO$_4$-50 | 318 | glass carbon | 0.26 | [39] J. Mater. Chem. A 2018, 6, 1639-1647. |
| Ni-BDC@NiS | 330 at 20 mA cm$^{-2}$ | Ni substrate | 0.20 | [40] ACS Appl. Mater. Interfaces 2019, 11, 41595-41601. |
| MOFs: NNU-23 | 365 | carbon cloth | 1.0 | [41] Angew. Chem. Int. Ed. 2018, 57, 9660-9664. |
| Co-MOF/GF | 220 | graphite foam | 3.2 | [42] Chem. Eur. J. 2018, 24, 18413-18418. |
| Ru@IrO$_x$ | 282 | gold electrode | 0.051 | [43] Chem 2019, 5, 445-459. |
| F-NiFe-A | 218 | nickel foam | 3.0 | [44] Nano Lett. 2021, 21, 492-499. |
| Ultrathin CoMn LDH nanosheets | 324 | glass carbon | 0.14 | [45] J. Am. Chem. Soc. 2014, 136, 16481-16484. |
| NiCo LDH@ZIF-67-VO/NF | 290 | nickel foam | - | [46] J. Mater. Chem. A 2019, 7, 4950-4959. |
| NC-Co$_3$O$_4$-90 | 358 | carbon cloth | 1.2 | [47] Adv. Mater. 2017, 29, 1704117. |
| NiFe LDH hollow nanoprisms | 280 | glass carbon | 0.16 | [48] Angew. Chem. Int. Ed. 2018, 57, 172-176. |
| Co/Co$_3$S$_2$@SNCF-800 | 306 | glass carbon | 0.40 | [49] ACS Appl. Mater. Interfaces 2017, 9, 34269-34278. |
| FeCo–N–C-700 | 380 | glass carbon | 0.40 | [50] J. Mater. Chem. A 2020, 8, 9355-9363. |
| CoZn-NC-700 | 390 | glass carbon | 0.24 | [51] Adv. Funct. Mater. 2017, 27, 170795. |
| α-phase Ni(OH)$_2$ | 340 | FTO | 0.05 | [52] Chem. Mater. 2020, 32, 10394-10406 |
| CoFe20@CC | 291 | glass carbon | 0.40 | [53] Adv. Mater. 2019, 31, 1904689. |
| Co$_3$O$_4$/HNCP-40 | 333 | glass carbon | 0.20 | [54] ACS Catal. 2018, 8, 7879-7888. |
| A$_2$B-MOF-FeCo$_{1.6}$ | 288 | glass carbon | 0.35 | [55] Adv. Energy Mater. 2018, 8, 1801564. |
| Ni|Fe-[TA]-Catalyst | QCM gold substrate | This work |
|---|---|---|
| ~349 | 0.01 | |
| ~321 | 0.01 | |
| ~313 | 0.01 | |
| ~309 | 0.01 | |
Table S3. ICP-OES data of the contents of Ni and Fe in electrolyte after alkali solution immersion for 3 min and on the electrode after OER process.

| Electrolyte | Contents of Ni and Fe | The electrolyte after 3 min immersion | Catalyst on the electrode | Atom ratio of Ni and Fe |
|-------------|-----------------------|--------------------------------------|---------------------------|-------------------------|
| LiOH        | Fe / at.%             | 1.39                                 | 98.61                     | ~3.9                    |
|             | Ni / at.%             | 0.76                                 | 99.24                     |                         |
| NaOH        | Fe / at.%             | 1.15                                 | 98.85                     | ~4.1                    |
|             | Ni / at.%             | 0.26                                 | 99.74                     |                         |
| KOH         | Fe / at.%             | 0.66                                 | 99.34                     | ~4.1                    |
|             | Ni / at.%             | 0.75                                 | 99.25                     |                         |
| CsOH        | Fe / at.%             | 1.22                                 | 98.78                     | ~4.2                    |
|             | Ni / at.%             | 0.44                                 | 99.56                     |                         |
| Samples                      | C-O | O=O-C | Ni(Fe)-OH | Ni(Fe)-O |
|-----------------------------|-----|-------|-----------|----------|
| Ni|Fe-[TA]-SURMOFs              | 532.91 | 30.6    | 531.99 | 34.7 | 530.72 | 18.5 | 529.72 | 16.2 |
| Ni|Fe-[TA]-Catalyst in LiOH     | 532.36 | 13.7    | 531.68 | 18.5 | 530.51 | 44.4 | 528.60 | 23.4 |
| Ni|Fe-[TA]-Catalyst in NaOH     | 532.19 | 6.4     | 531.28 | 18.0 | 530.46 | 43.3 | 529.34 | 32.3 |
| Ni|Fe-[TA]-Catalyst in KOH      | 532.69 | 16.3    | 531.95 | 22.9 | 530.80 | 42.5 | 530.08 | 18.3 |
| Ni|Fe-[TA]-Catalyst in CsOH     | 532.65 | 21.8    | 532.02 | 19.3 | 531.01 | 42.3 | 529.69 | 16.6 |
Table S5. The coordination bond lengths of the cation (M)-oxygen (O) obtained from DFT calculations. M-O bonds can be divided into two types, i.e., M-OH$_2$ in hydrated shells and M-O connected with the lattice oxygen in the surface layer of NiFe(OOH). These bond length results were obtained from the average values of the corresponding bond lengths in a unit cell lattice model.

| M-O coordination bond length (Å) | Li$^+$ | Na$^+$ | K$^+$ | Cs$^+$ |
|---------------------------------|-------|-------|-------|--------|
| M-OH$_2$ (hydrated water)       | 2.11  | 2.52  | 2.90  | 3.07   |
| M-O (lattice)                   | 2.21  | 2.43  | 2.83  | 3.15   |
[50] X. Duan, S. Ren, N. Pan, M. Zhang, H. Zheng, *J. Mater. Chem. A* **2020**, *8*, 9355-9363.

[51] B. Chen, X. He, F. Yin, H. Wang, D.-J. Liu, R. Shi, J. Chen, H. Yin, *Adv. Funct. Mater.* **2017**, *27*, 1700795.

[52] D. Böhm, M. Beetz, C. Kutz, S. Zhang, C. Scheu, T. Bein, D. Fattakhova-Rohlfing, *Chem. Mater.* **2020**, *32*, 10394-10406.

[53] C.-C. Hou, L. Zou, Q. Xu, *Adv. Mater.* **2019**, *31*, 1904689.

[54] D. Ding, K. Shen, X. Chen, H. Chen, T. Fan, R. Wu, Y. Li, *ACS Catal.* **2018**, *8*, 7879-7888.

[55] Z. Xue, Y. Li, Y. Zhang, W. Geng, B. Jia, J. Tang, S. Bao, H.-P. Wang, Y. Fan, Z.-w. Wei, Z. Zhang, Z. Ke, G. Li, C.-Y. Su, *Adv. Energy Mater.* **2018**, *8*, 1801564.