Supporting Information

The 3d-5d orbital repulsion of transition metals in oxyhydroxide catalysts facilitates water oxidation

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Abstract: The electrocatalytic oxygen-evolution reaction (OER) is expected to play a vital role in the development of electrochemical energy conversion and storage technologies. The 3d transition-metal oxyhydroxides have been reported to outperform noble metal-based catalysts for OER, but the relatively localized property of 3d electrons limits the sufficient modulation of their electronic structures by dopants, which may inhibit further improvement of their OER performances. Herein, through density functional theory (DFT) calculation, we found that 5d transition metals such as iridium (Ir) with unique electronic properties can effectively modulate 3d transition-metal oxyhydroxides, thus producing versatile electronic structures to facilitate the OER activity. We therefore synthesized NiFe(3d)Ir(5d) oxyhydroxides and explored their electronic structures via in-situ and ex-situ X-ray absorption spectroscopy (XAS) and valence band X-ray photoelectron spectroscopy (VB-XPS). The DFT, XAS, VB-XPS and electrochemistry studies demonstrated that Ir served as a modulator in 3d metal oxyhydroxide framework, which created a local environment favoring 3d-5d orbital interaction, and the repulsed Ni 3d orbits facilitated electron transfer from reactants to active sites. The Ir-doped catalyst on glassy carbon electrode delivers 133 mV lower overpotential to reach a current density of 10 mA cm⁻² in alkaline electrode, a 54-fold improvement turnover frequency (TOF) over that of pristine NiFe oxyhydroxides, with negligible activity decay after 500 hours of operation.
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**Experimental Section**

**Computational details.**
All density functional theory calculations mentioned in this manuscript were implemented by the Vienna ab initio simulation package (VASP) version 5.4.1. The projected augmented wave method with a cut-off energy of 400 eV in real space was utilized to treat the solution of single-electron wavefunction. The formula of Perdew-Burke-Ernzerhof functional was adopted to describe the exchange-correction energy under the generalized gradient-corrected approximation. The threshold of force and energy convergence was set to 0.05 eV/Å and 10⁻⁴ eV, respectively, for geometry optimization at ground state. Furthermore, DFT-D3 Grimme method was taken into consideration to describe the weak van der Waals interaction.

The free energy change (ΔG) in an elementary reaction was calculated by

\[ \Delta G = \Delta E + \Delta ZPE - T \Delta S \]

where the ΔE, ΔZPE, and TΔS represent the difference of total energy, zero-point energy, and entropy between the initial state and final states, respectively. T is the reaction temperature (300 K). All DFT calculations in our manuscript were based on the most stable adsorption configurations of the OER intermediates, instead of the transition states. And the theoretical onset overpotential was calculated by the formula:

\[ \eta = \text{max}[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4, \Delta G_5] / e - 1.23 \text{ [V]} \]

where ΔG₁, ΔG₂, ΔG₃, ΔG₄ and ΔG₅ represented the free energy difference of the OER intermediates at every step shown in Figure 1.

Considering the electrons involved in the entire reaction in the electrode, the standard hydrogen electrode (SHE) model was adopted in our system and the energy of (H⁺+e⁻) or adsorbed H was approximated by the half energy of hydrogen (H₂) in the gas phase.

**Materials.**
Nickel chloride hexahydrate (NiCl₂·6H₂O), iron chloride hexahydrate (FeCl₃·6H₂O), Sodium hexachloroiridate hexahydrate (Na₂IrCl₆·6H₂O), Iridium chloride (IrCl₃), ethanol (≥99.5%), propylene oxide (≥99%), Nafion (5wt%) were obtained from Sigma-Aldrich. Acetone was purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without any further purification. For X-ray absorption spectroscopy (XAS) measurements, Ni foil, Fe foil and Pt foil were provided by the beamline, nickel(II) oxide (NiO, 99.99%), nickel(III) oxide (Ni₂O₃, 99%), iron(III) oxide (Fe₂O₃, 99.99%), iridium(III) chloride (IrCl₃, anhydrous, 99.99%) were purchased from Macklin Inc.

**Synthesis of catalysts.**
All catalysts were synthesized using a sol-gel method. In a typical synthesis of NiFeIr catalysts, NiCl$_2$·6H$_2$O (2.2 mmol), FeCl$_3$·6H$_2$O (0.25 mmol), Na$_2$IrCl$_6$·6H$_2$O (0.25 mmol) were first dissolved in ethanol (4 mL) to form Solution A. Deionized water (0.18 mL) was added in ethanol (2 mL) to form Solution B. Both Solution A and B were cooled in an ice bath for 2 h. Then, propylene oxide (1 mL) and Solution B were slowly added to Solution A under magnetic stirring to form a brown gel. The gel was aged for 1 day, and then immersed in acetone for 5 days. After that, the gel were centrifuged at 6000 rpm for collection, and then washed with acetone for several times. Resulting products were annealed at 350 °C for 2 h in air to obtain the NiFeIr catalyst. For the synthesis of NiFe, NiIr, NiFeIr-H and IrO$_2$ catalysts, different mole ratios of Ni/Fe/Ir salts (9:1:0, 9:0:1, 1:1:9 and 0:0:1) were added at the beginning with the total amount of metal ions (Ni$^{2+}$ + Fe$^{3+}$ + Ir$^{4+}$) kept at 2.7 mmol. To produce the NiFeIr-RT catalyst, the centrifuged products were vacuum dried directly.

**Morphology study of catalysts.**

The high-resolution transmission electron microscopy (HR-TEM) image and energy disperse x-ray spectrometry (EDS) mapping were obtained from a JOEL-2100F TEM equipped with an Oxford energy disperse spectrometer. The powder X-ray diffraction (XRD) patterns were measured on a Bruker D8 Advance spectrometer. The actual molar ratios of as-prepared catalysts were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP7400, Thermo Fisher). The actual molar ratios for NiFe, NiFeIr, and NiFeIr-RT were 0.91:0.09 (Ni:Fe), 0.83:0.08:0.08 (Ni:Fe:Ir) and 0.84:0.08:0.07 (Ni:Fe:Ir), respectively.

**Electrochemical measurements.**

Electrochemical measurements were performed using a three-electrode system at a potentiostat (Metrohm Autolab M204), using saturated Ag/AgCl electrode as the reference electrode and platinum foil as the counter electrode. To prepare the catalysts deposited on the glassy carbon electrode (GCE, 3 mm in diameter), 10 mg of catalyst was dispersed in 1.25 mL mixture of water and ethanol (4:1, v/v), and then 80 µL of 5wt% Nafion solution was added. The suspension was immersed in an ultrasonic bath for at least 30 min to obtain a homogeneous ink. After that, 5 µL of the catalyst ink was carefully deposited onto the GCE (catalyst loading 0.53 mg cm$^{-2}$). During electrochemical testing, the working electrode was cycled at a rate of 50 mV s$^{-1}$ until achieving stable cyclic voltammetry scans. Linear sweep voltammetry with rate of 5 mV s$^{-1}$ was conducted in 1 M KOH (pH=13.6) at room temperature. All potentials were reference to reversible hydrogen electrode (RHE) by following calculations:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \times pH$$

The Faradaic efficiency (η) was calculated by the formula:
\[ \eta = \frac{zFn}{Q} \]

Where \( z \), \( F \), \( n \), and \( Q \) represent the number of electrons transferred, the Faraday constant (96485 C mol\(^{-1}\)), the number of moles of \( \text{O}_2 \), and the total charge during electrolysis, respectively. Electrochemical impedance spectra (EIS) measurements were conducted at a bias of 1.45V, 1.48V and 1.50V vs. RHE in the frequency range from 10 kHz to 100 Hz with amplitude of 5 mV. All the potentials and voltages were 95\% iR-corrected unless noted.

**Calculation of electrochemically active surface area.**

To calculate the electrochemically active surface area (ECSA), cyclic voltammetry (CV) measurements were firstly carried out to test the electrochemical double layer capacities (\( C_{dl} \)) at the range of 0-0.1 V vs. Ag/AgCl. The \( C_{dl} \) was estimated by plotting the difference in current density between the anodic and the cathodic sweep at a 0.05 V against the scan rate (Figures S31 and S32). EIS fittings were also carried out to estimate the value of \( C_{dl} \) as a reference (Figure S28). The ECSA was calculated by the formula \( \text{ECSA} = \frac{C_{dl}}{C_s} \), where \( C_s \) is the capacitance of the atomically smooth planar surface of the material per unit area under identical electrolyte condition. Here, a value of 0.040 mF cm\(^{-2}\) was adopted from previous reports.\(^6\), \(^7\)

**The fitting of EIS spectra.**

The EIS fitting was carried out based on the equivalent circuit demonstrated in Figure S26, which was widely adopted in the analysis of OER electrocatalysts.\(^8\)-\(^10\) As show in Figures 4c and S25-29, two semi-circles were obtained in these spectra. At low frequency range, uncompensated solution resistance (\( R_\Omega \)), double layer capacitance (\( C_{dl} \)) and interfacial charge transfer resistance (\( R_{ct} \)) should be considered in the fitting. In addition, the high frequency semicircle was attributed to the resistance (\( R_{film} \)) and dielectric properties (\( C_{film} \)) of the catalysts film. These features were clearer in the Bode plots (Figure S27). The impedance modulus (left axis) of NiFeIr and NiFeIr-RT consisted of three plateaus and two slopes from high frequency region to low frequency region, representing \( R_\Omega \), \( R_{film} \), \( R_{ct} \), \( C_{film} \) and \( C_{dl} \), respectively, where \( R_\Omega \) was uncompensated solution resistance, \( R_{film} \) was resistance of catalysts’ film, \( R_{ct} \) was interfacial charge transfer resistance, \( C_{film} \) was the dielectric properties of film and \( C_{dl} \) was double layer capacitance. While the \( R_{film} \) term in NiFe was obviously larger (clearly identified from the maximum in the phase curve), indicating an unfavorable conductivity of the NiFe film.

**Calculation of turnover frequency (TOF).**
Turnover frequency (TOF) is defined as the frequency of reaction on per active site, which is used to compare the intrinsic activity of different catalysts. For OER, TOF value is usually calculated by the equation:

$$\text{TOF} = \frac{j \times A \times \eta}{4 \times F \times n}$$

Where $j$ is the current density at overpotential = 300 mV after 95% iR-compensation. $A$ is the geometric area of glassy carbon electrode (0.071 cm$^2$). $\eta$ is the Faradic efficiency and $F$ is Faraday’s constant. $n$ is the molar number of active site. In our study, we assumed Ni as active sites (except for IrO$_2$), and the number of $n$ were estimated by two methods:

The first method is calculated via the total loading mass, which is an underestimated way, according to equation:

$$n_{\text{mass}} = \frac{m_{\text{loading}} \times N_A}{M_w}$$

Where $m_{\text{loading}}$ is the loading mass via drop-casting. The chemical formula was defined as (Ni$_{0.82}$Fe$_{0.09}$Ir$_{0.09}$)O$_{1.55}$ for NiFeIr and NiFeIr-RT, for example. $N_A$ is Avogadro’s constant and $M_w$ is the molecular weight of catalysts.

The second method is estimating the active site number via ECSA,$^{11}$ which is more accurate but several cell parameters need to be determined before calculation. The value of ECSA normalized active site number is calculated via the following equation:

$$n_{\text{ECSA}} = \frac{ECSA \times c_{\text{cell}} \times n_{\text{cell}}}{v_{\text{cell}} \times N_A}$$

In this equation, ECSA is the electrochemical surface area, $v_{\text{cell}}$, $c_{\text{cell}}$ and $n_{\text{cell}}$ are the volume of the unit cell, the c axis length of the unit cell and the number of metal atoms per unit cell, respectively. For NiFe, NiFeIr and NiFeIr-RT, the crystal structure of NiOOH$^{12}$ is used as the model structure, in which $v_{\text{cell}} = 47.41$ Å$^3$, $c_{\text{cell}} = 6.88$ Å (interlayer spacing of the layered double hydroxide) and $n_{\text{cell}} = 1$ Ni atoms per unit cell. As to the IrO$_2$,$^{13}$ model, the three parameters are 63.68 Å$^3$, 3.15 Å and 2 Ir atoms per unit cell, respectively.

**Valence-band X-ray photoelectron spectroscopy (VB-XAS) measurements and analysis**

The VB-XPS measurements were conducted on a PHI 5300 X-ray photoelectron spectrometer, with a monochromatic Mg Ka X-ray sources (1253.6 eV). The samples (NiFe, NiFeIr and NiFeIr-RT, all loaded on carbon paper) were first reacted at OER condition (1.5 V vs. RHE) for 15 min. After reaction, the samples were gently washed by DI water, dried in vacuum, and then put into the vacuum chamber of XPS as soon as possible. The scanning ranges from -5 eV to 25 eV at a step of 0.2 eV. The scan was performed for 20 times. The binding energy of all samples was corrected according to
C 1s peak (284.6 eV). The baselines of VB-XPS spectra were fitted by Shirley curves (Figure S22).

The measurements of regular Ni 2p spectra were also carried out. The spectra and fits were presented in Figure S17. By comparing the spectrum of NiFe and NiFeIr, a valence increase of Ni could be observed after introducing Ir, and the Ni valence of NiFeIr-RT was even higher.

**X-ray absorption spectroscopy (XAS) measurements and analysis.**

Ni, Fe K-edge absorption spectra were performed on the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF), China. The monochromator energy was calibrated with Ni and Fe foil rising edge energy, respectively. The Ir L₃-edge absorption spectra were performed on the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF), China. The monochromator energy was calibrated with a Pt foil rising edge energy. All spectra were collected in fluorescent mode. The spectra were obtained from 8.1 keV to 9.1 keV for Ni K-edge XAS, 6.8 keV to 7.7 keV for Fe K-edge XAS, and 11 keV to 12 keV for Ir L-edge XAS at 0.5 eV steps at the near edge. For *ex-situ* samples, the samples were prepared by loading catalyst samples on carbon paper after reaction for 30 min at 1.5 V vs. RHE in the chemistry laboratory of synchrotron facilities and took to the beamline immediately for measurements. For *in-situ* samples, the experiment was conducted in a home-made triangular electrochemical cell, and working electrodes were prepared by loading catalyst samples on carbon paper. The electrochemical cell was placed in the middle of the optical path with an incident angle of 45°. During the *in-situ* measurements, chronoamperometry processes at 1.5 V vs. RHE were employed. For the standard samples, all samples were prepared by being uniformly placed on 3M tape.

All XAS data were processed by *Athena* software included in *Demeter* software package.¹⁴ For Ni K-edge data, the absorption edge energy E₀ of pure Nickel foil was aligned to 8333 eV. E₀ of Nickel foil was assigned by the first maximum of first-derivative X-ray absorption near edge structure (XANES) spectrum. All data was aligned according to the standard Nickel foil. For Ir L₃-edge data, a Pt foil was used as standard sample. The E₀ of Pt L₃-edge was assigned to 11564 eV. All Ir L₃-edge data was calibrated according to the standard Pt sample. For Fe K-edge data, the energy was calibrated to 7112 eV according to a standard Fe foil.

Due to self-absorption effects of fluorescents in heavy metal, nickel might absorb the fluorescents emitted from iridium centers, which will attenuate the XANES and extended X-ray absorption fine structure (EXAFS) spectra of iridium.¹⁵ Therefore, we
utilized the self-absorption correction program included in *Athena* software to correct the XANES and EXAFS spectra of low Ir-doped NiFeIr prior to data analysis.\textsuperscript{14} The correction was conducted according to the chemical formula \((\text{Ni}_{0.82}\text{Fe}_{0.09}\text{Ir}_{0.09})\text{O}_{1.55}\cdot \text{C}_{71}\), where \(\text{C}_{71}\) was calculated according to the density of carbon paper substrate and loading amount of catalysts.

The simulation of EXAFS spectra of NiFeIr, IrO\(_2\) and *in situ* NiFeIr-RT sample were carried out by the FEFF6 codes embedded in the *Artemis* software. The crystallographic information file (CIF) of IrO\(_2\),\textsuperscript{13} NiOOH,\textsuperscript{12} and NiO\(_2\)\textsuperscript{16} were used as models to calculate raw scattering paths. The experimental spectra were fitted by raw scattering paths at a \(k\)-range of 3 to 12 Å\(^{-1}\), selected path and fitting parameters were presented in Table S1. We first compared the structures of our electrocatalysts before and after OER with the simulation spectra of NiO and NiOOH (Figures S18-20). Phase transformations could be observed in NiFeIr and NiFeIr-RT, which coincided with the previous reports of 3d transition metal oxide electrocatalysts.\textsuperscript{17} These results indicated that 3d metal oxyhydroxides are the active phases, so we focused on the post-OER samples. As to the coordination numbers of NiFeIr and NiFeIr-RT, two schematics were presented in Figure S35 to illustrate the local environment of NiFeIr catalysts. In Ni K-edge EXAFS, the second coordination shell of central Ni atom included 6 Ni atoms, where one of them was replaced by Ir or Fe, so the fitted coordination number of the second shell Ni was \(~5.87\) (with an uncertainty of \(\pm 1.01\)) while the second shell Ir was \(~2.55\) statistically (with an uncertainty of \(\pm 1.14\)). While in Ir L\(_3\)-edge EXAFS, the second coordination shell of central Ir atom should be consistent with 6 Ni atom, so the fitted coordination number of the second shell Ni was \(6.29\) (with an uncertainty of \(\pm 2.12\)).

For the Ir L\(_3\)-edge white-line analysis, the white-line position shifts were identified by the “white-line search” program embedded in *Athena* software. Assuming the formal d-electron hole value of metallic Ir powder (5d\(^7\)), IrCl\(_3\) (5d\(^8\)) and IrO\(_2\) (5d\(^5\)), we can plot a calibration line by white-line position versus formal d-electron hole numbers. The slope of which is 1.292, similar with the literature reports\textsuperscript{18-20}. The formal d-electron hole numbers of NiFeIr was also calculated, featuring NiFeIr \(\approx 4.82\) d-electron holes (Figure S1). This indicate that NiFeIr had a nominal oxidation state of +3.82.

Under the assumption that the \(L_3:L_2\) ratio remains fixed, which is reasonable for oxidized iridium,\textsuperscript{20} the integral area of the \(L_3\) white-line is proportional to the number of d-electron holes. To identify the number of d-electron holes in different sample, the Ir L\(_3\)-edges were fitted with an arctangent function and a Lorentzian function to account for the transition to continuum and the transition to the bound state,
respectively (Figure S5). The calculated area was presented in Figure S6. The area of NiFeIr is extraordinarily high, which means the electronic nature of iridium in NiFeIr is different from other iridium samples. So the second derivative spectra was introduced to uncover the buried information (Figure S7).\textsuperscript{21} Two splitting negative-going peaks could be well-resolved in the second-derivative spectra, except for IrCl\textsubscript{3}.\textsuperscript{22} According to crystal field theories of octahedral symmetry, this splitting can be attributed to t\textsubscript{2g} (d\textsubscript{xy}, d\textsubscript{xz} and d\textsubscript{yz}) and e\textsubscript{g} (d\textsubscript{x\textsuperscript{2}} and d\textsubscript{y\textsuperscript{2}}\textsuperscript{−}x\textsuperscript{2}) states.\textsuperscript{21} The low energy peak refers to the probability of 2p \textendash t\textsubscript{2g} transitions, while the high energy peak refers to the probability of 2p \textendash e\textsubscript{g} transitions. In the case of Ir(III)Cl\textsubscript{3} (5d\textsuperscript{6}), the possible electronic configuration would be t\textsubscript{2g}\textsuperscript{6}e\textsubscript{g}\textsuperscript{0}, in which only e\textsubscript{g} states have the possibility of transition, this could explain why IrCl\textsubscript{3} has only one peak in second-derivate spectrum. Meanwhile, in the case of Ir(IV) (5d\textsuperscript{5}), two possible configurations exists. They are low-spin state t\textsubscript{2g}\textsuperscript{5}e\textsubscript{g}\textsuperscript{0} and high-spin state t\textsubscript{2g}\textsuperscript{3}e\textsubscript{g}\textsuperscript{2}. In IrO\textsubscript{2}, the t\textsubscript{2g} and e\textsubscript{g} peaks were of the similar area, indicating a high-spin d-electron configurations. However, in NiFeIr sample, the e\textsubscript{g} absorption peak was obviously larger than t\textsubscript{2g} band, which means that Ir at modulating sites possessed a low-spin d-electron configurations.
Supplementary Figures S1-S35

Figure S1. TEM images and EDS mapping of NiFe. a), b) TEM images of NiFe. c) STEM image and corresponding distributions of elements.
Figure S2. TEM images and EDS mapping of NiFeIr. a), b) TEM images of NiFeIr. c) STEM image and corresponding distributions of elements.
Figure S3. TEM images of IrO$_2$. 
Figure S4. White-line position of NiFeIr (pentastar) as a function of the formal d-electron hole numbers. Formal d-electron hole values were calculated based on the white-line shift and the increase of 1.292 eV per d-electron hole calibrated from iridium powder (5d$^7$), IrCl$_3$ (5d$^6$) and IrO$_2$ (5d$^5$) standards.
Figure S5. Lorentzian area fits of different iridium catalysts.
Figure S6. Integrated white-line area of different samples.
Figure S7. Second derivative of Ir L$_3$-edge XANES of different samples.
Figure S8. a) EXAFS spectra of Ni K-edge plotted in k-space, with k-weight = 2. b) Fourier-transformed EXAFS spectra of Ni K-edge plotted in R-space, with k-weight = 2.
Figure S9. a) EXAFS spectra of Ir L$_3$-edge plotted in k-space, with k-weight = 2. b) Fourier-transformed EXAFS spectra of Ir L$_3$-edge plotted in R-space, with k-weight = 2.
Figure S10. Fe K-edge XANES spectra before (a) and after (b) OER reaction.
Figure S11. a) EXAFS spectra of Fe K-edge plotted in k-space, with k-weight = 2. b) Fourier-transformed EXAFS spectra of Fe K-edge plotted in R-space, with k-weight = 2.
**Figure S12.** Three independent OER polarization curves of different electrocatalysts on GCE in three-electrode configuration in 1 M KOH aqueous electrolyte with scan rate 5 mV s\(^{-1}\) at room temperature.
**Figure S13.** TEM images and EDS mapping of NiFeIr-RT. a), b) TEM images of NiFeIr-RT. c) STEM image and corresponding distributions of elements.
Figure S14. XRD patterns and corresponding PDF cards of different as-prepared electrocatalysts: a) NiFe, b) NiFeIr, c) IrO$_2$ and d) NiFeIr-RT.
Figure S15. a) The Ni K-edge XANES spectra of *ex situ* NiFeIr, NiFeIr-RT and *in situ* NiFeIr-RT at a bias of 1.5V vs. RHE. b) The experimental and fitted EXAFS spectra of *in situ* NiFeIr-RT.
Figure S16. Ni K-edge XANES spectra of NiFeIr-RT before and after OER. The as-prepared NiFeIr-RT demonstrated a valence of Ni(III), while the Ni(IV) was generated after OER.
**Figure S17.** a) Normalized Ni 2p XPS spectra of NiFe, NiFeIr and NiFeIr-RT after baseline subtraction. b), c) and d) The fitting of the above spectra, respectively.
Figure S18. The Ni K-edge EXAFS spectra of NiFe before and after OER, together with a simulation spectrum of NiO calculated by FEFF.
**Figure S19.** The Ni K-edge EXAFS spectra of NiFeIr before and after OER, together with simulation spectra of NiO and NiOOH calculated by FEFF.
Figure S20. The Ni K-edge EXAFS spectra of NiFeIr-RT before and after OER, together with a simulation spectra of NiOOH calculated by FEFF.
Figure S21. a) The Ir L₃-edge XANES spectra of ex situ NiFeIr, NiFeIr-RT and standard samples. b) The second derivative XANES spectra of NiFeIr and NiFeIr-RT.
Figure S22. The VB-XPS spectra of NiFe, NiFeIr and NiFeIr-RT after baseline subtraction. Inset: the normalized VB-XPS spectra and the fitted baseline.
Figure S23. The Fe K-edge XANES spectra of *in situ* NiFeIr-RT at a bias of 0 V and 1.5 V vs. RHE.
Figure S24. Fe K-edge XANES spectra of NiFeIr-RT before and after OER process.
Figure S25. The full view of Nyquist plots for different electrocatalysts recorded at 1.48V vs. RHE.
Figure S26. The equivalent circuits used in EIS fitting, where $R_\Omega$ is uncompensated solution resistance, $R_{ct}$ is the charge transfer resistance, $C_{dl}$ is the double layer capacitance, and $R_{\text{film}}$ and $C_{\text{film}}$ are the resistivity and dielectric properties of the oxide film, respectively.
Figure S27. The Bode plots of EIS spectra measured at 1.48V vs. RHE: a) NiFe, b) NiFeIr, c) IrO₂ and d) NiFeIr-RT.
Figure S28. The full picture of EIS spectra, together with the corresponding fitted spectra: a) NiFe, b) NiFeIr, c) IrO$_2$ and d) NiFeIr-RT.
Figure S29. EIS spectrum measured at different potentials: a) NiFe, b) NiFeIr, c) IrO₂ and d) NiFeIr-RT. For NiFeIr-RT, the spectrum of 1.50V vs. RHE was not measured due to vigorous bubbling.
**Figure S30.** Cyclic voltammograms of different electrocatalysts of NiFe (a), NiFeIr (b), IrO$_2$ (c) and NiFeIr-RT (d) at different scan rates (from 10 to 50 mV/s with an increment of 10 mV/s).
Figure S31. Scan rate dependence of the current density for different electrocatalysts at 0.05 V vs. Ag/AgCl.
Figure S32. Intrinsic activities of different electrocatalysts (normalized by electrochemical surface area obtained from cyclic voltammetry).
Figure S33. OER activity comparison between NiFeIr, NiFe and NiIr in 1M KOH. It can be found that NiIr outperformed NiFe, which meant that Ir incorporation had a stronger effect than that of Fe, and the synergy of Ir and Fe can further improve the performance.
Figure S34. The OER polarization curves for Ir-dominated electrocatalyst in 1 M KOH solution. The NiFeIr-H required overpotential of 309 mV to achieve a current density of 10 mA cm$^{-2}$, significantly higher than those of NiFeIr (255 mV). This result suggests that the low content of Ir can achieve a better interaction with Ni.
Figure S35. The schematic of Ni-O-Ir local structures.
**Supplementary Tables S1-S4**

*Table S1.* Parameters used in EXAFS fittings.

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<th>Sample</th>
<th>Element</th>
<th>Path</th>
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<th>$S_0^2$</th>
<th>$\sigma^2$</th>
<th>$E_0$</th>
<th>$R$</th>
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<td>Ir</td>
<td>Ir-O</td>
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<td></td>
<td>Ir-Ni</td>
<td>6.29±2.12</td>
<td>5.28</td>
<td>0.011</td>
<td>8.46</td>
<td>3.04±0.03</td>
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<tr>
<td>IrO₂</td>
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<td>Ir-O</td>
<td>5.93±0.98</td>
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<td>0.0047</td>
<td>11.09</td>
<td>1.98±0.01</td>
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<tr>
<td></td>
<td></td>
<td>Ir-Ir</td>
<td>5.59±3.38</td>
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<td>Ir-Ir</td>
<td>4.41±3.38</td>
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<td></td>
<td></td>
<td>Ni-Ni</td>
<td>5.87±1.01</td>
<td>3.99</td>
<td>0.0057</td>
<td>-5.70</td>
<td>2.83±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni-Ir</td>
<td>2.55±1.14</td>
<td>1.74</td>
<td>0.0057</td>
<td>4.90</td>
<td>2.86±0.03</td>
</tr>
</tbody>
</table>
Table S2. Summary of parameters used in EIS fittings.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>NiFe</th>
<th>NiFeIr</th>
<th>IrO₂</th>
<th>NiFeIr-RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_\Omega$ (Ω)</td>
<td>7.36</td>
<td>7.10</td>
<td>9.74</td>
<td>7.38</td>
</tr>
<tr>
<td>$R_{ct}$ (Ω)</td>
<td>562.70</td>
<td>75.35</td>
<td>652.20</td>
<td>26.28</td>
</tr>
<tr>
<td>$C_{dl}$ (mF)</td>
<td>0.91</td>
<td>5.20</td>
<td>2.48</td>
<td>6.42</td>
</tr>
<tr>
<td>$C_{dl,N}$</td>
<td>0.77</td>
<td>0.92</td>
<td>0.91</td>
<td>0.86</td>
</tr>
<tr>
<td>$R_{film}$ (Ω)</td>
<td>97.72</td>
<td>10.48</td>
<td>7.11</td>
<td>2.38</td>
</tr>
<tr>
<td>$C_{film}$ (mF)</td>
<td>0.87</td>
<td>4.90</td>
<td>30.53</td>
<td>0.089</td>
</tr>
<tr>
<td>$C_{film,N}$</td>
<td>0.52</td>
<td>0.33</td>
<td>0.42</td>
<td>0.84</td>
</tr>
</tbody>
</table>
Table S3. Summary of electrochemical characterizations of different samples.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>NiFe</th>
<th>NiFeIr</th>
<th>IrO₂</th>
<th>NiFeIr-RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_\Omega$ (Ω)</td>
<td>7.36</td>
<td>7.10</td>
<td>9.74</td>
<td>7.38</td>
</tr>
<tr>
<td>$R_{ct}$ (Ω)</td>
<td>562.70</td>
<td>75.35</td>
<td>652.20</td>
<td>26.28</td>
</tr>
<tr>
<td>$C_{dl}^1$ (mF cm$^{-2}$)</td>
<td>12.96</td>
<td>74.23</td>
<td>35.40</td>
<td>91.71</td>
</tr>
<tr>
<td>ECSA$^2$ (cm$^2$)</td>
<td>22.67</td>
<td>129.90</td>
<td>61.95</td>
<td>160.50</td>
</tr>
<tr>
<td>$C_{dl}^3$ (mF cm$^{-2}$)</td>
<td>0.35</td>
<td>0.66</td>
<td>144.00</td>
<td>0.32</td>
</tr>
<tr>
<td>ECSA$^4$ (cm$^2$)</td>
<td>0.63</td>
<td>1.17</td>
<td>256.00</td>
<td>0.57</td>
</tr>
<tr>
<td>TOF$^5$ (s$^{-1}$)</td>
<td>0.00085</td>
<td>0.015</td>
<td>0.0043</td>
<td>0.044</td>
</tr>
<tr>
<td>TOF$^6$ (s$^{-1}$)</td>
<td>0.0065</td>
<td>0.019</td>
<td>0.013</td>
<td>0.045</td>
</tr>
<tr>
<td>TOF$^7$ (s$^{-1}$)</td>
<td>0.24</td>
<td>2.09</td>
<td>0.0036</td>
<td>12.69</td>
</tr>
<tr>
<td>Tafel slope (mV dec$^{-1}$)</td>
<td>75.00</td>
<td>68.00</td>
<td>80.10</td>
<td>64.30</td>
</tr>
<tr>
<td>Overpotential$^8$ (mV, iR-corrected)</td>
<td>340</td>
<td>255</td>
<td>323</td>
<td>207</td>
</tr>
</tbody>
</table>

1 $C_{dl}$ were obtained from EIS at 1.48V.
2 Calculated according to $C_{dl}$ obtained from EIS.
3 $C_{dl}$ were calculated by the cyclic voltammetry methods at non-Faradic region.
4 Calculated according to $C_{dl}$ obtained from cyclic voltammetry.
5 Calculated according to mass loading of all atoms.
6 Calculated according to ECSA obtained from EIS.
7 Calculated according to ECSA obtained from cyclic voltammetry.
8 Overpotential at 10 mA cm$^{-2}$. 
Table S4. The comparison of OER overpotentials to reach the current density of 10 mA cm\(^{-2}\) on the glassy carbon electrode of our catalyst with other superior selected catalysts in 1 M KOH.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Overpotential at 10 mA cm(^{-2}) (mV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe-GO</td>
<td>210</td>
<td>23</td>
</tr>
<tr>
<td>CoFe LDHs</td>
<td>232</td>
<td>24</td>
</tr>
<tr>
<td>Ni-Bi@NB</td>
<td>302</td>
<td>25</td>
</tr>
<tr>
<td>NiFeS</td>
<td>230</td>
<td>26</td>
</tr>
<tr>
<td>CoMn LDH</td>
<td>293</td>
<td>27</td>
</tr>
<tr>
<td>NiFe LDH</td>
<td>260</td>
<td>28</td>
</tr>
<tr>
<td>MoO(_2)-CoO-C</td>
<td>270</td>
<td>29</td>
</tr>
<tr>
<td>CoSe(_2)</td>
<td>320</td>
<td>30</td>
</tr>
<tr>
<td>NiFe/NC</td>
<td>330</td>
<td>31</td>
</tr>
<tr>
<td>CoP/Cu</td>
<td>345</td>
<td>32</td>
</tr>
<tr>
<td>CoO(_x)</td>
<td>325</td>
<td>33</td>
</tr>
<tr>
<td>Ni-Fe LDH hollow nanoprisms</td>
<td>280</td>
<td>34</td>
</tr>
<tr>
<td>SnCoFe-Ar</td>
<td>300</td>
<td>35</td>
</tr>
<tr>
<td>CoFe(_2)O(_4) NSs</td>
<td>275</td>
<td>36</td>
</tr>
<tr>
<td>NCoM-Cb-Ar</td>
<td>340</td>
<td>37</td>
</tr>
<tr>
<td>NiFeIr-RT</td>
<td>207</td>
<td>This work</td>
</tr>
</tbody>
</table>
References