Supporting Information

Preferential Co substitution on Ni sites in Ni-Fe oxide arrays enabling large-current-density alkaline oxygen evolution

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Experimental Section

Chemicals
Ni(NO$_3$)$_2$•6H$_2$O ($\geq 99.0\%$, AR), Co(NO$_3$)$_2$•6H$_2$O ($\geq 99.0\%$, AR), FeSO$_4$•7H$_2$O ($\geq 99.0\%$, AR), NaCl ($\geq 99.0\%$, AR), RuO$_2$ (99.9%), H$_2$SO$_4$ and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. Nafion solution (5 wt %) was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Ni foam was purchase from Shenzhen Meisen electromechanical equipment Co., Ltd. All of the reagents were used without further purification.

Materials Synthesis

Synthesis of Co-NiO/Fe$_2$O$_3$ Nanosheet Arrays

In this experiment, Ni foam with geometric area of 2×2 cm$^2$ was firstly washed by acetone, ethanol, and H$_2$SO$_4$ aqueous solution (2.0 M), respectively. For the synthesis of Co-NiO/Fe$_2$O$_3$ catalyst, the pre-cleaned Ni foam and the mixed solution (20 mL) containing Co(NO$_3$)$_2$•6H$_2$O (12.5 mM) and FeSO$_4$•7H$_2$O (12.5 mM) were successively transferred to a 50 mL Teflon-lined autoclave and kept at 80 °C for 12 hrs. Then, the sample was washed with deionized water and absolute ethanol for several times to get hydroxide nanosheet precursors after drying overnight at 60 °C. Subsequently, the Co-NiO/Fe$_2$O$_3$ was obtained by calcination the above precursor in air at 450 °C for 2 hrs. The mass loading of the catalysts supported on Ni foam substrate are around 2.15 mg cm$^{-2}$.

Synthesis of NiO/Fe$_2$O$_3$ Nanosheet Arrays

The NiO/Fe$_2$O$_3$ nanosheet arrays were prepared by the same procedure for the Co-NiO/Fe$_2$O$_3$ nanosheet arrays except that Ni(NO$_3$)$_2$•6H$_2$O (12.5 mM) to replace Co(NO$_3$)$_2$•6H$_2$O (12.5 mM).

Materials Characterizations

The composition and structure of the as-prepared samples were examined by X-ray diffraction (XRD) on a X-ray diffractometer (SmartLab, Rigaku, Japan) using a Cu K$_\alpha$ radiation source ($\lambda = 0.154178$ nm). Field-emission scanning electron microscope (FESEM) (SU8020, Hitachi, Japan) and transmission electron microscope (TEM) (JEM-1400flash, JEOL, Japan) images of the
samples were obtained to characterize the morphology and microstructure. The thickness of the sample was measured by atomic force microscopy (AFM) (Dimension Icon, Bruker, Germany). Elemental mapping and select area electron diffraction (SAED) patterns of the samples were taken on a field-emission transmission electron microscope (FETEM) (JEM-2100F, JEOL, Japan). The valence state of the samples was recorded by X-ray photoelectron spectroscopy (XPS) (ESCALAB250Xi, Thermo, America) equipped with a hemispherical energy analyzer and a monochromatic Al Kα source.

**Electrochemical Measurements**

All electrochemical measurements were carried out on an electrochemical workstation (CHI 760E) via a conventional three-electrode system in 1.0 M O₂-saturated KOH media under ambient conditions. 1 M KOH + 0.5 M NaCl and 1 M KOH + seawater were used to evaluate the OER performance for actual industrial application and the natural seawater was collected from Bohai Sea, China. A Pt net (1×1.5 cm²), an Hg/HgO electrode, and the as-prepared catalysts were employed as the counter, reference electrode and working electrode, respectively. The linear sweep voltammetry (LSV) curves were collected at a scan rate of 5 mV s⁻¹ with 90% iR compensation. The Cₐl values were evaluated based on cyclic voltammetry (CV) curves under non-Faradaic region. Electrochemical impedance spectroscopy (EIS) was investigated in an O₂-saturated electrolyte with amplitude of 5 mV and the frequency range from 10 kHz to 0.01 Hz. The multicurrent processes and chronopotentiometry curve were investigated without iR compensation.

For comparison, the RuO₂, NiO, Fe₂O₃ were evaluated. The working electrodes of these catalysts were prepared by dispersing 2 mg powders into a water–ethanol solution containing 10 μL Nafion, respectively, and sonicating for 1 h to form a homogeneous catalyst inks. Then the catalyst ink was cast onto Ni foam and dried in air at room temperature.

**Density Functional Theory Calculations**

Quantum espresso (QE) based on the pseudopotential plane wave (PPW) method was used to complete density functional theory (DFT) calculations. The perdew-Bueke-Ernzerhof (PBE) functional was employed to describe exchange-correlation effects of electrons. Projected augmented wave (PAW) potentials were chose to describe the ionic cores and take valence
electrons into account using a plane wave basis set with a kinetic energy cutoff of 500 eV.\textsuperscript{4,5} Slab models were built by slicing (111) and (110) planes of NiO and Fe\textsubscript{2}O\textsubscript{3} respectively to model the surfaces of materials. An extra vacuum of 12 Å were applied along z-direction to avoid interactions. In order to specify the most stable doping sites for Co, different possible sites were calculated in NiO and Fe\textsubscript{2}O\textsubscript{3}, where the most stable ones were used to carry out further simulation. Further, to explore the effects of NiO/Fe\textsubscript{2}O\textsubscript{3}, heterojunction models were built considering both un-doped and Co-doped structures. All of the structures were first optimized to reach their most stable configuration. All of the atom positions were allowed to relax during the geometry optimizations. The Brillouin-zone sampling was conducted using Monkhorst-Pack (MP) grids of special points with the separation of 0.04 Å\textsuperscript{-1}.\textsuperscript{6} The convergence criterion for the electronic self-consistent field (SCF) loop was set to $1 \times 10^{-5}$ eV/atom. The atomic structures were optimized until the residual forces were below 0.05 eV Å\textsuperscript{-1}. Based on the relaxed structures, free energy along OER reaction path was calculated. The d-band center was calculated based on the following equation:

$$\epsilon = \frac{\int_{-\infty}^{E_f} E f_d(E) dE}{\int_{-\infty}^{E_f} f_d(E) dE}$$

Where $f_d$ represent the density of states (DOS) of the specified orbital.

Differential charge density was calculated by $D_{\text{diff}} = D_{\text{tot}} - D_{\text{sub}} - D_{\text{abs}}$, where $D_{\text{tot}}$, $D_{\text{sub}}$, and $D_{\text{abs}}$ were charge density of whole system, density of substrate and density of absorbed molecules respectively.
Fig. S1a reveals the formation of 3Ni(OH)$_2$$\cdot$2H$_2$O and FeOOH precursors after hydrothermal reaction containing both Co$^{2+}$ and Fe$^{2+}$. The formation of FeOOH may be due to that the hydrolysis product Fe(OH)$_2$ could be easily oxidized to FeOOH by the dissolved oxygen. Furthermore, the Co signals could be detected in the XPS spectra although the corresponding diffraction peaks related to Co could not observed in the XRD patterns for the precursors. The high-resolution Co 2p and Ni 2p spectra of the precursors can be assigned to Ni$^{2+}$, Ni$^{3+}$ and Co$^{2+}$, Co$^{3+}$, respectively, and Fe 2p regions can be fitted into a pair of Fe$^{3+}$ peaks and satellite peaks in the precursors (Fig. S1b-d).
Fig. S2 (a-b) FESEM images of pure Ni foam. (c-d) FESEM images, (e) SEM and (f) the corresponding EDS spectrum of the obtained Ni foam after hydrothermal reaction of Ni foam and FeSO$_4$ aqueous solution (without the addition of Co(NO$_3$)$_2$).

When only Ni foam and FeSO$_4$ are added into the hydrothermal system, as shown in the Fig. S2, the FESEM images exhibit that no nanosheets or other nanostructures are observed on the surface of the skeleton of smooth Ni foam, which is also confirmed by EDS results, suggesting that the co-deposition reaction cannot occur without Co$^{2+}$ ions assistance.
Fig. S3 (a) XRD pattern, (b) survey XPS spectrum and high resolution (c) Fe 2p and (d) Ni 2p XPS spectra for the obtained Ni foam after hydrothermal reaction of Ni foam and FeSO₄ aqueous solution (without the addition of Co(NO₃)₂).

In the absence of Co²⁺, only the diffraction peaks of Ni foam substrate could be observed after hydrothermal reaction (Fig. S3a), and no nanosheet arrays or other nanostructures could be observed on Ni foam (Fig. S2). Besides, the survey and Fe/Ni 2p XPS spectra confirm the existence of Ni and O elements while Fe signals could not be detected (Fig. S3b-d).
**Fig. S4** The pH values of the solution for the synthesis of hydroxide precursors in hydrothermal reaction.
Co(NO$_3$)$_2$$\cdot$6H$_2$O and Ni foam were used to prepare Co-Ni based hydroxides under hydrothermal condition. Then, the hydroxide precursors were further treated in air at 450 °C for 2 hrs. Crystalline Co$_3$O$_4$ and NiO phases could be detected in the XRD pattern. In contrast, no crystalline Co$_3$O$_4$ could be found in the Co-NiO/Fe$_2$O$_3$. This suggests that substitutional incorporation of Co into the lattices of NiO or Fe$_2$O$_3$ may occur during the heat treatment of Fe-Co-Ni based hydroxide precursors.

Fig. S5 XRD pattern of NiO/Co$_3$O$_4$. 
Fig. S6 The top views of (a) pure NiO and (b) pure Fe$_2$O$_3$. 
The XRD pattern of NiO/Fe$_2$O$_3$ is refined, which confirms that the as-prepared NiO/Fe$_2$O$_3$ also consists of NiO, Fe$_2$O$_3$, and Ni compared with the Co-NiO/Fe$_2$O$_3$ (Ni was peeled from Ni foam.)
Fig. S8 (a, b) FESEM images and (c) EDS spectrum of the obtained precursor after hydrothermal reaction of Ni foam, Co(NO$_3$)$_2$ and FeSO$_4$.

The Fe-Co-Ni based precursors exhibit typical vertically arrayed nanosheet morphology with Ni, Co, Fe and O elements.
Fig. S9 (a) FESEM image, (b) EDS spectrum, and (c) elemental mapping images of the NiO/Fe$_2$O$_3$.

We used the similar method to prepare the Ni and Fe based precursors with the addition of Ni$^{2+}$ instead of Co$^{2+}$ in the hydrothermal reaction. The obtained precursors were then calcined at the same condition. The resulting NiO/Fe$_2$O$_3$ also maintains the morphology of nanosheets and shows uniform elemental distribution.
Fig. S10 (a) Polarization curves and (b) long-term stability tests at a constant current density of 500 mA cm$^{-2}$ for the Co-NiO/Fe$_2$O$_3$ electrode in different electrolytes.

Alkaline simulated seawater (1 M KOH + 0.5 M NaCl) and alkaline natural seawater (1 M KOH + seawater) electrolytes were used to further evaluate the OER performance of the Co-NiO/Fe$_2$O$_3$. The Co-NiO/Fe$_2$O$_3$ shows overpotentials of 265 and 300 mV at 100 mA cm$^{-2}$ in alkaline simulated seawater, and 313 and 373 mV at 500 mA cm$^{-2}$ in alkaline natural seawater. The Co-NiO/Fe$_2$O$_3$ also maintains stable potentials at 500 mA cm$^{-2}$ under continuous operation for 50 hrs both in either alkaline simulated seawater or alkaline natural seawater.
CV curves of different catalysts under various scan rates (40 to 180 mV s\(^{-1}\)). (a) NiO, (b) Fe\(_2\)O\(_3\), (c) NiO/Fe\(_2\)O\(_3\), (d) Co-NiO/Fe\(_2\)O\(_3\).

CV curves of different catalysts NiO, Fe\(_2\)O\(_3\), NiO/Fe\(_2\)O\(_3\) and Co-NiO/Fe\(_2\)O\(_3\) have been added as shown in Fig. S11. We calculated the C\(_{dl}\) values of different electrocatalysts based on these CV curves and further estimated the electrochemical surface areas for different electrocatalysts. The C\(_{dl}\) values were calculated to be 0.69, 0.64, 1.86 and 3.16 mF cm\(^{-2}\) for NiO, Fe\(_2\)O\(_3\), NiO/Fe\(_2\)O\(_3\), and Co-NiO/Fe\(_2\)O\(_3\), respectively, suggesting that the Co-NiO/Fe\(_2\)O\(_3\) can offer more abundant active sites as well as higher interfacial contact areas.
Fig. S12 Linear sweep voltammetry curves normalized by electrochemical double-layer capacitance.

To further evaluate the intrinsic catalytic activity of all the catalysts, the electrochemical double layer capacitance ($C_{dl}$) normalized linear scanning voltammetry (LSV) curves were collected. The Co-NiO/Fe$_2$O$_3$ requires only 204 mV overpotential to reach 10 A F$^{-1}$, which is significantly lower than those for the NiO, Fe$_2$O$_3$ and NiO/Fe$_2$O$_3$, demonstrating the high intrinsic OER activity of the Co-NiO/Fe$_2$O$_3$ with Co substitution.
Fig. S13 Overpotentials at current densities of 100, 200, and 500 mA cm$^{-2}$ for seven Co-NiO/Fe$_2$O$_3$ electrodes prepared in seven parallel experiments.

Seven Co-NiO/Fe$_2$O$_3$ electrodes exhibit nearly identical potentials at 100, 200 and 500 mA cm$^{-2}$ in seven parallel experiments, demonstrating the superb reproducibility in this work.
Fig. S14 The calculated DOS for (a) NiO and (b) Co doped NiO.

Fig. S14 shows partial DOS plots before and after Co substitution. Asymmetric DOS is observed due to magnetic Ni atoms. Pure Ni has a wide band gap of the electrons (0.80 eV) and has a semiconducting band structure, showing a semiconductor nature. After Co substitution, a significantly narrower band gap of 0.42 eV is observed for Co doped NiO, revealing the highly improved electronic conductivity of the Co-NiO/Fe$_2$O$_3$. 
**Fig. S15** FESEM images and EDS spectra of the Co-NiO/Fe$_2$O$_3$ before (a, b) and after (c, d) chronopotentiometry at 500 mA cm$^{-2}$ for 300 hrs.

After long-term OER measurement, the morphology of Co-NiO/Fe$_2$O$_3$ remains the original nanosheet structure, revealing the high stability of the electrode. EDS spectrum of the Co-NiO/Fe$_2$O$_3$ after chronopotentiometry was further measured to investigate the reason for the slight stability degradation. As shown in Fig. S15d, EDS results confirm the presence of Ni, Co, and Fe after OER stability test. However, the atomic ratio of Co and Fe elements in the Co-NiO/Fe$_2$O$_3$ decreases to 2.2 and 8.4 at %, respectively. Co and Fe elements play an important role in the improvement of electrocatalytic performance of the Co-NiO/Fe$_2$O$_3$. The Co and Fe leaching during OER process may cause the slight stability degradation in a long-term stability test.
Fig. S16 XPS spectra of the Co-NiO/Fe$_2$O$_3$ before and after chronoamperometric operation. (a) survey, (b) Ni 2p, (c) Co 2p and (d) Fe 2p XPS spectra.

XPS spectra of the Co-NiO/Fe$_2$O$_3$ were collected to show the differences before and after stability test. Obviously, the results verify the presence of Ni, Co and Fe after OER stability test and show that the relative intensities of Ni$^{3+}$ and Co$^{3+}$ peaks are significantly increased, indicating that Ni and Co are oxidized to higher valence states which are considered as the real active sites in the previous reported results.
**Fig. S17** Electrocatalytic activity for overall water splitting in 1.0 M KOH aqueous solution. (a) LSV polarization curves of the Co-NiO/Fe$_2$O$_3$ || commercial Pt/C cell and the commercial RuO$_2$ || Pt/C cell. (b) Long-term stability test of the Co-NiO/Fe$_2$O$_3$ || commercial Pt/C cell at constant current densities of 500 mA cm$^{-2}$.

The LSV polarization curve of the Co-NiO/Fe$_2$O$_3$ || Pt/C cell reveals that a low voltage of 1.64 V is required to reach 500 mA cm$^{-2}$, while the voltage of commercial RuO$_2$ || Pt/C cell is 1.65 V at a low current density of 10 mA cm$^{-2}$ (Fig. S17a), suggesting the superior activity of the Co-NiO/Fe$_2$O$_3$ in overall water splitting. Furthermore, the Co-NiO/Fe$_2$O$_3$ || Pt/C cell exhibits high stability for electrolysis of water at 500 mA cm$^{-2}$, and the voltage of the cell only increases from 1.64 to 1.72 V after OER test for 50 hrs (Fig. S17b).
Fig. S18  $\Delta G$ of four elementary reactions ($M \rightarrow \cdot \text{OH} \rightarrow \cdot \text{O} \rightarrow \cdot \text{OOH} \rightarrow \text{O}_2$) for OER at Ni and Fe sites on surface model of NiO/Fe$_2$O$_3$ and Co-NiO/Fe$_2$O$_3$.

The elementary reaction with maximum change of $\Delta G$ is identified as rate-determining step (RDS) in the OER process. The second step from $\cdot \text{OH}$ to $\cdot \text{O}$ on the Ni and Fe sites in the NiO/Fe$_2$O$_3$ and Co-NiO/Fe$_2$O$_3$ has the lowest $\Delta G$ value and could be considered as RDS in our work. Co substitution in the Co-NiO/Fe$_2$O$_3$ reduces the energy barriers of RDS for both Ni (from 1.31 eV to 1.26 eV) and Fe (from 1.74 eV to 1.68 eV) sites, which contributes to the enhancement of OER activity.
**Fig. S19** Projected density of states (PDOS) of Fe $d$ orbitals for (a) NiO/Fe$_2$O$_3$ and (b) Co-NiO/Fe$_2$O$_3$ at $^*$$\text{OH}$ intermediates.

The $d$-band center of Ni is -5.5427 eV and that of Fe is -7.1802 eV with respect to the Fermi energy level in the Co-NiO/Fe$_2$O$_3$. For the NiO/Fe$_2$O$_3$, the $d$-band center of Ni is -5.8353 eV and that of Fe is -7.3221 eV relative to the Fermi energy level. The $d$-band centers of Ni and Fe in the Co-NiO/Fe$_2$O$_3$ are closer to the Fermi energy level, implying the better OER activity after Co substitution.
**Table S1.** Lattice and structure parameters of the Co-NiO/Fe$_2$O$_3$ from XRD Rietveld refinement.

| Phase No. | Fe$_2$O$_3$  | Ni    | Co-NiO |
|-----------|-------------|-------|--------|
| Space group | R-3c        | Fm-3m | R-3m  |
| a(Å)      | 5.0415(11)  | 3.52544 | 2.9556(20) |
| b(Å)      | 5.0415(11)  | 3.52544 | 2.9556(20) |
| c(Å)      | 13.7574(62) | 3.52544 | 7.2271(13) |
Table S2. Lattice and structure parameters of the NiO/Fe$_2$O$_3$ from XRD Rietveld refinement.

| Phase No. | Fe$_2$O$_3$ | Ni | NiO |
|-----------|-------------|----|-----|
| Space group | R-3cH | Fm-3m | R-3mH |
| a(Å) | 5.0489(23) | 3.5238 | 2.950(15) |
| b(Å) | 5.0489(23) | 3.5238 | 2.950(15) |
| c(Å) | 13.7568(77) | 3.5238 | 7.240(75) |
Table S3. OER performances of the Co-NiO/Fe\textsubscript{2}O\textsubscript{3} compared with other advanced transition metal-based electrocatalysts in 1.0 M KOH alkaline solution.

| Catalysts | Current density [mA cm\textsuperscript{-2}] | Overpotential [mV] | Tafel slope [mV dec\textsuperscript{-1}] | Stability | Reference |
|-----------|---------------------------------|----------------|-------------------------------|----------|-----------|
| Co-NiO/Fe\textsubscript{2}O\textsubscript{3} | 100 500 | 220 230 | 33.9  250 | 300h@500 mA cm\textsuperscript{-2} | This work |
| NiCo\textsubscript{2},Fe\textsubscript{2}O\textsubscript{4} | 10 | 274 | 42 | 25h@10 mA cm\textsuperscript{-2} | 7 |
| CeO\textsubscript{2},-FeNi | 10 | 195 | 43 | 48h@10 mA cm\textsuperscript{-2} | 8 |
| FeCoSeO\textsubscript{4} | 10 | 294 | 45.1 | 40h@10 mA cm\textsuperscript{-2} | 9 |
| Cu@CeO\textsubscript{2}@NiFeCo-0.25 | 10 | 230 | 32.7 | 30h@10 mA cm\textsuperscript{-2} | 10 |
| Fe–Co–O/Co@NC-mNS/NF | 10 | 257 | 41.56 | 50h@10 mA cm\textsuperscript{-2} | 11 |
| CoNiFeO\textsubscript{-NC} | 100 | 286 | 64.05 | 40h@1.49V | 12 |
| NiFe\textsubscript{2}O\textsubscript{4}–NMO-25 | 100 | 304 | 42.7 | 40 h@200 mA cm\textsuperscript{-2} | 13 |
| CoNi/CoFe\textsubscript{2}O\textsubscript{4}/NF | 100 | 290 | 45 | 48 h@100 mA cm\textsuperscript{-2} | 14 |
| Ir-NiO | 10 | 215 | 38 | 10 h@10 mA cm\textsuperscript{-2} | 15 |
| Fe-NiO-Ni CHNAs | 10 | 245 | 43.4 | 24 h@10 mA cm\textsuperscript{-2} | 16 |
| Co\textsubscript{3}O\textsubscript{4}/CoO | 10 | 302 | 68.6 | 4*10\textsuperscript{4} s@10 mA cm\textsuperscript{-2} | 17 |
| CoVFeN@NF | 10 | 212 | 34.8 | 50h@100 mA cm\textsuperscript{-2} | 18 |
| (Ni\textsubscript{i},Fe\textsubscript{1-i})\textsubscript{P} | 10 100 | 166 250 | 59.3 24h@10 mA cm\textsuperscript{-2} | 24h@100 mA cm\textsuperscript{-2} | 19 |
| Cu@NiFe LDH | 10 | 199 | 27.8 | 48h@10 mA cm\textsuperscript{-2} | 20 |
| Ni\textsubscript{5}Co\textsubscript{3}Mo-OH | 100 | 281 | 56.4 | 100h@100 mA cm\textsuperscript{-2} | 21 |
| Ni\textsubscript{3}S\textsubscript{2}/MnO\textsubscript{2} | 10 100 | 260 348 | 61 48 h@100 mA cm\textsuperscript{-2} | 22 |
| e-ICLDH@GDY/NF | 100 | 249 | 43.6 | 80 h@100 mA cm\textsuperscript{-2} | 23 |
| S-doped (Ni,Fe)OOH | 100 | 281 | 48.9 | 100 h@100 mA cm\textsuperscript{-2} | 24 |
| NiMoO\textsubscript{2}/NiMoS | 100 | 225 | 34 | 25 h@100 mA cm\textsuperscript{-2} | 25 |
Table S4. The EIS fitting data of different catalysts at 1.47 V (vs RHE).

| Sample          | $R_s$[Ω] | $R_{ct}$[Ω] | CPE,$\Delta F$ |
|-----------------|----------|-------------|-----------------|
| Co-NiO/Fe$_2$O$_3$ | 1.028    | 1.015       | 0.5262          |
| NiO             | 3.078    | 7.818       | 0.6797          |
| Fe$_2$O$_3$     | 1.618    | 5.834       | 0.7246          |
| NiO/Fe$_2$O$_3$ | 1.642    | 1.823       | 0.5580          |
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