# Strong Electronic Interaction in P and Fe Dual-doped Co<sub>3</sub>O<sub>4</sub> Nano-network Structure Supported on 3D Ni Foam for Highly Efficient Overall Water Splitting

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# **1.** Calculation of turnover frequency (TOF)

The TOF value reflects the intrinsic activity of the catalyst<sup>[1-3]</sup>. The specific calculation process is as follows:

In 1.0 M KOH, the voltammetric charge (anode and cathode) of the active component are recorded on the CV curve between 0 V and 0.05 V at a scan rate of 8 mV s<sup>-1</sup>. The number of active sites (n) of the catalyst in the non-Faraday region can be obtained from the formula below:

$$n = \frac{Q}{2F}$$

F: Faraday constant (96485 C mol<sup>-1</sup>), Q: Whole charge of CV curve (C).

When the number of active sites is acquired, the following formula is used to calculate the replacement frequency of each site (unit: s<sup>-1</sup>):

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$$TOF = \frac{I}{4nF}$$

I: Current during the linear sweep measurement (A) at a given overpotential, n: Number of active sites (mol)

## 2. Experimental section

## 2.1. Preparation of Co<sub>3</sub>O<sub>4</sub>@NF

 $Co_3O_4$  nanoneedles were in situ grown on nickel foam (NF) by a hydrothermal and heat treatment method. Initially,  $Co(NO_3)_2 \cdot 6H_2O(0.14 \text{ mmol})$  and  $CO(NH_2)_2(1.4 \text{ mmol})$  were thoroughly dissolved in deionized water (70 mL), and this homogenous solution, along with the pre-cleaned NF, was transferred to a Teflon-lined autoclave (100 mL) and maintained at 120 °C for 6 h. Subsequently, the pink precursor grown on NF was rinsed three times with anhydrous ethanol and deionized water respectively, then dried at 60 °C overnight. Ultimately, the precursor was annealed in air at 350 °C for 2 h, followed by cooling to room temperature, thereby yielding the  $Co_3O_4@NF$ .

### 2.2. Preparation of Fe-Co<sub>3</sub>O<sub>4</sub>@NF

The preparation conditions for all samples were identical to those used for  $Co_3O_4@NF$ , with the sole variation being the introduction different amounts of FeSO<sub>4</sub> into the reaction mixture. The samples produced were named as 5-Fe-Co<sub>3</sub>O<sub>4</sub>@NF, Fe-Co<sub>3</sub>O<sub>4</sub>@NF, and 10-Fe-Co<sub>3</sub>O<sub>4</sub>@NF, according to the respective percentages of FeSO<sub>4</sub> added (5 %, 7 %, and 10 % relative to Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O at 0.14 mmol).

#### 2.3. Preparation of P-Co<sub>3</sub>O<sub>4</sub>@NF

The pre-prepared  $Co_3O_4$ @NF and  $NaH_2PO_2$  were positioned in a tubular furnace, downstream and upstream, respectively. Then, they are subjected to a thermal treatment at 300 °C for 30 min with a heating rate of 2 °C min<sup>-1</sup>, under Ar atmosphere which acts as the carrier gas. Following this treatment, the system can be cooled to room temperature. The obtained catalyst, named P100-Co<sub>3</sub>O<sub>4</sub>@NF, P-Co<sub>3</sub>O<sub>4</sub>@NF, and P200-Co<sub>3</sub>O<sub>4</sub>@NF, correspond to the amount of  $NaH_2PO_2$  used (100, 150, and 200 mg, respectively).

#### 2.4. Preparation of P-Fe-Co<sub>3</sub>O<sub>4</sub>@NF

The fabrication process for P-Fe-Co<sub>3</sub>O<sub>4</sub>@NF is the same as that for P-Co<sub>3</sub>O<sub>4</sub>@NF, with the distinction that Fe-Co<sub>3</sub>O<sub>4</sub>@NF is utilized in place of Co<sub>3</sub>O<sub>4</sub>@NF.

#### 2.5. Preparation of IrO<sub>2</sub> and Pt/C electrode

Uniform ink was prepared by dispersing 10 mg  $IrO_2$  powder and 50 µL nafion in 450 µL anhydrous ethyl alcohol, followed by ultrasonication for 1 h to ensure a homogeneous mixture. This catalyst ink was then coated on the clean NF substrate to fabricate the  $IrO_2$  electrode, with a loading of approximately 1.0 mg cm<sup>-2</sup>. Subsequently, the electrodes were left to dry overnight at 60 °C.

The synthesis method of Pt/C follows the same procedure as that of  $IrO_2$ , with the only difference being the substitution of  $IrO_2$  with Pt/C.

#### 2.6. Materials characterization

Morphology characterization was acquired by Hitachi S-4800 scanning electron microscope (SEM). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were performed with Tecnai<sup>™</sup> G2 F30 instrument. X-ray diffraction (XRD) patterns were obtained using Malvern Panalytical EMPYREAN multipurpose X-ray diffractometer with a Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was carried out on Kratos AXIS Ultra DLD apparatus.

#### 2.7. Electrochemical measurement

All electrochemical measurements were conducted on the CHI 760E work station using a typical three-electrode device in 1.0 M KOH solution. The prefabricated samples ( $1 \times 1 \text{ cm}^2$ ) were used as a working electrode, graphite rod and Hg/HgO were served as counter electrode and reference electrode, respectively. Linear sweep voltammograms (LSV) was applied to evaluate electrochemical performance at a scanning rate of 5 mV s<sup>-1</sup>, with the potential measurements calibrated by 90% iR compensation. Electrochemical impedance spectroscopy (EIS) was carried out with a frequency range of  $10^{-2}$  to  $10^{5}$  Hz at a voltage of 0.6 V. Cyclic voltammetry (CV) was employed to measure the electrochemical bilayer capacitance in the non-Faraday region, which reckoned the effective electrochemical surface area (ECSA). All stability was evaluated by chronoamperometry. The overall water splitting measurements were executed in a two-electrode system, with the as-prepared electrocatalysts as both the cathode and anode.

## 3. Density functional theory (DFT) calculations

In order to investigate in depth the underlying causes of the differences in electrocatalytic performance of catalyst materials, we have performed spin-polarized density generalized theoretical calculations using Vienna ab initio Simulation Package  $(VASP)^{[4.6]}$ . The effect of exchange correlation energy is described by the PBE function<sup>[7,8]</sup>. The projector augmented wave (PAW) potentials that describes interaction between ion cores and valence electrons are used with a cutoff energy of 520 eV<sup>[9]</sup>. The structural relaxation convergence criterion is a system energy change of less than  $10^{-5}$  eV, and the ion position optimization convergence criterion is a residual force on the atom of less than 0.03 eV<sup>[10]</sup>. The k-point grid size is  $3 \times 2 \times 1^{[10]}$ . To avoid strong interactions between atoms caused by periodic mirroring in the cell, we add a vacuum layer of 15 Å. We use the GGA+U model developed by Dudarev to describe the strong correlation system because of the strong in-situ Coulomb repulsion between the d electrons of Co atom and Fe atom, and the U value of Co atom and Fe atom are both  $3^{[11]}$ .

In this work, the properties of the surface are studied using (110) surface simulations of  $\text{Co}_3\text{O}_4^{[12]}$ . The surface model contains five layers, of which the lower three are fixed and the upper two are released. The iron and phosphorus atoms at the doping sites are placed as close to the cobalt atoms as possible to allow the maximum effect of heteroatom doping.

In an alkaline environment, the OER reaction usually undergoes a four-step association mechanism<sup>[13]</sup>:

$$OH^- + * \rightarrow *OH + e^-$$
 (S1)

$$*OH + OH^{-} \rightarrow *O + H_2O + e^{-}$$
(S2)

$$*O + OH^{-} \rightarrow *OOH + e^{-}$$
(S3)

$$*OOH + OH^{-} \rightarrow O_2 + H_2O + e^{-} + *$$
 (S4)

Where \* and \*M represent the adsorption active sites and various adsorption intermediates of the surface, respectively.

The adsorption free energy of each step of the reaction can be expressed as:

$$\Delta G = \Delta E_{ads} + \Delta E_{ZPE} - T\Delta S \tag{S5}$$

Where  $\Delta E_{ZPE}$ ,  $\Delta S$  are the zero-point vibrational energy and the entropy contribution to the free energy change, respectively.

$$\Delta E_{OH} = E(*OH) - E(*) - [E(H_2O) - 1/2 E(H_2)]$$
(S6)

$$\Delta E_{O} = E(*O) - E(*) - [E(H_{2}O) - E(H_{2})]$$
(S7)

$$\Delta E_{OOH} = E(*OOH) - E(*) - [2E(H_2O) - 3/2 E(H_2)]$$
(S8)

The Gibbs free energy changes of OER can be expressed as:

$$\Delta G_1 = \Delta G_{*OH} - eU \tag{S9}$$

$$\Delta G_2 = \Delta G_{*O} - \Delta G_{*OH} - eU \tag{S10}$$

$$\Delta G_3 = \Delta G_{*OOH} - \Delta G_{*O} - eU \tag{S11}$$

$$\Delta G_4 = 4.92 - \Delta G_{*OOH} - eU \tag{S12}$$

Where U is the potential obtained by measuring an ordinary hydrogen electrode under standard conditions.

For OER, the theoretical overpotential is calculated from the rate determining step:

$$\eta = \max \left[ \Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4 \right] / e - 1.23 \text{ V}$$
(S13)

The formula for calculating the d-band center  $(\epsilon_d)$  is as follows:

$$\varepsilon_{\rm d} = \frac{\int_{-\infty}^{+\infty} {\rm ED}(E) dE}{\int_{-\infty}^{+\infty} {\rm D}(E) dE}$$
(S14)

Where E is the energy level of the electronic state, and D(E) is the density of states corresponding to the energy level of the transition metal d state.



Figure S1. a-d) SEM images of Co<sub>3</sub>O<sub>4</sub>@NF, 5-Fe-Co<sub>3</sub>O<sub>4</sub>@NF, Fe-Co<sub>3</sub>O<sub>4</sub>@NF, and 10-Fe-

Co<sub>3</sub>O<sub>4</sub>@NF, respectively.



Figure S2. XRD patterns of Co<sub>3</sub>O<sub>4</sub>@NF, Fe-Co<sub>3</sub>O<sub>4</sub>@NF, P-Co<sub>3</sub>O<sub>4</sub>@NF, and P-Fe-

Co<sub>3</sub>O<sub>4</sub>@NF.



Figure S3. N<sub>2</sub> adsorption-desorption isotherm curves: a) Co<sub>3</sub>O<sub>4</sub>@NF, b) P-Fe-Co<sub>3</sub>O<sub>4</sub>@NF; average pore size: c) Co<sub>3</sub>O<sub>4</sub>, d) P-Fe-Co<sub>3</sub>O<sub>4</sub>@NF.



Figure S4. a) TEM image and b) HR-TEM image of Co<sub>3</sub>O<sub>4</sub>@NF. c) STEM image. d) and e)

Elemental mapping images for Co and O, respectively.



Figure S5. a) TEM image and b) HR-TEM image of Fe-Co<sub>3</sub>O<sub>4</sub>@NF. c) STEM image. d-f) Elemental mapping images for Co, Fe and O, respectively.



Figure S6. a) TEM image and b) HR-TEM image of Fe-Co<sub>3</sub>O<sub>4</sub>@NF. c) STEM image. d-f)





Figure S7. a) OER polarization curves, b) Tafel slopes of Co<sub>3</sub>O<sub>4</sub>@NF, 5-Fe-Co<sub>3</sub>O<sub>4</sub>@NF, Fe-

Co<sub>3</sub>O<sub>4</sub>@NF, and 10-Fe-Co<sub>3</sub>O<sub>4</sub>@NF.



Figure S8. EIS of Co<sub>3</sub>O<sub>4</sub>@NF, 5-Fe-Co<sub>3</sub>O<sub>4</sub>@NF, Fe-Co<sub>3</sub>O<sub>4</sub>@NF, and 10-Fe-Co<sub>3</sub>O<sub>4</sub>@NF.



Figure S9. a-d) CV curves of the Co<sub>3</sub>O<sub>4</sub>@NF, 5-Fe-Co<sub>3</sub>O<sub>4</sub>@NF, Fe-Co<sub>3</sub>O<sub>4</sub>@NF, and10-Fe-

Co<sub>3</sub>O<sub>4</sub>@NF in 1.0 M KOH electrolyte at a scan rate from 2 to 10 mV s<sup>-1</sup>.



Figure S10. C<sub>dl</sub> of Co<sub>3</sub>O<sub>4</sub>@NF, 5-Fe-Co<sub>3</sub>O<sub>4</sub>@NF, Fe-Co<sub>3</sub>O<sub>4</sub>@NF, and 10-Fe-Co<sub>3</sub>O<sub>4</sub>@NF.



Figure S11. a) Reverse sweep OER polarization curves, b) Tafel slopes of Co<sub>3</sub>O<sub>4</sub>@NF, P100-Co<sub>3</sub>O<sub>4</sub>@NF, P-Co<sub>3</sub>O<sub>4</sub>@NF, and P200-Co<sub>3</sub>O<sub>4</sub>@NF.



Figure S12. a-d) CV curves of the  $Co_3O_4$ @NF, Fe-Co<sub>3</sub>O<sub>4</sub>@NF, P-Co<sub>3</sub>O<sub>4</sub>@NF, and P-Fe-





Figure S13. Multistep chronoamperometry measurements of P-Fe-Co<sub>3</sub>O<sub>4</sub>@NF.



Figure S14. The SEM information of P-Fe-Co<sub>3</sub>O<sub>4</sub>@NF before and after i-t test.



Figure S15. a-b) The XRD and XPS spectrum of P-Fe-Co<sub>3</sub>O<sub>4</sub>@NF before and after i-t test.



Figure S16. The high resolution XPS spectra of P-Fe-Co<sub>3</sub>O<sub>4</sub>@NF before and after i-t test.



**Figure S17.** a) HER polarization curves, b) Tafel slopes of Co<sub>3</sub>O<sub>4</sub>@NF, 5-Fe-Co<sub>3</sub>O<sub>4</sub>@NF, Fe-Co<sub>3</sub>O<sub>4</sub>@NF, and 10-Fe-Co<sub>3</sub>O<sub>4</sub>@NF.



Figure S18. a) HER polarization curves, b) Tafel slopes of Co<sub>3</sub>O<sub>4</sub>@NF, P100-Co<sub>3</sub>O<sub>4</sub>@NF, P-Co<sub>3</sub>O<sub>4</sub>@NF, and P200-Co<sub>3</sub>O<sub>4</sub>@NF.



**Figure S19.** (a,c) Unit cell, (b,d) the bulk density of states of  $Co_3O_4$  and P-Fe-  $Co_3O_4@NF$ , where the blue, green, red and pink balls represent Co, Fe, O and P atoms, respectively.

	Co <sub>3</sub> O <sub>4</sub>	P-Co <sub>3</sub> O <sub>4</sub>	Fe-Co <sub>3</sub> O <sub>4</sub>	P-Fe-Co <sub>3</sub> O <sub>4</sub>
Со	38.1%	33.5%	35.8%	31.5%
0	61.9%	57.6%	61.4%	57.9%
Р	0	8.9%	0	8.2%
Fe	0	0	2.8%	2.4%

Table S1 The atomic ratio of all samples.

Samples	$\eta_{10} \left( mV \right)$	Tafel (mV dec $^{-1}$ )	Electrolyte
P-Fe-Co <sub>3</sub> O <sub>4</sub> @NF(this work)	250 (ŋ <sub>50</sub> )	24.37	1 M KOH
P-Co <sub>3</sub> O <sub>4</sub> /NiO <sup>[14]</sup>	293	77	1 M KOH
Co <sub>3</sub> O <sub>4</sub> /NiO@CeO <sub>2</sub> -2 HPN <sup>[15]</sup>	290	66	1 M KOH
P-Co <sub>3</sub> O <sub>4</sub> -V <sub>o</sub> <sup>[16]</sup>	276	96	1 M KOH
CoCe <sub>0.2</sub> HNFs <sup>[17]</sup>	315	87.6	1 M KOH
13.4 % Ni-Co <sub>3</sub> O <sub>4</sub> NFs <sup>[18]</sup>	420	97	$0.5 \text{ M H}_2\text{SO}_4$

Table S2 OER electrocatalytic activity data for most cobalt-based electrocatalysts.

 Table S3 HER electrocatalytic activity data for most cobalt-based electrocatalysts.

Samples	$\eta_{10}(mV)$	Electrolyte
P-Fe-Co <sub>3</sub> O <sub>4</sub> @NF(this work)	139.8	1 M KOH
CoSe <sub>2</sub> /Co <sub>3</sub> S <sub>4</sub> @Co <sub>3</sub> O <sub>4</sub> <sup>[19]</sup>	165	1 M KOH
Co <sub>3</sub> O <sub>4</sub> @MoO <sub>3</sub> <sup>[20]</sup>	158	1 M KOH
Co <sub>3</sub> O <sub>4</sub> /10 wt% C-dots <sup>[21]</sup>	383	1 M KOH
$Mn_{0.8}Co_{2.2}O_4/NF^{[22]}$	154	1 M KOH

 Table S4 overall water splitting electrocatalytic activity data for most cobalt-based
 electrocatalysts.

Samples	$\eta_{10}\left(V ight)$	Electrolyte
P-Fe-Co <sub>3</sub> O <sub>4</sub> @NF(this work)	1.44	1 M KOH
PtIr- $Co_3O_4^{[23]}$	1.57	1 M KOH
$W-Co_3S_4 @ Co_3O_4^{[24]}$	1.63	1 M KOH
Ru- Co <sub>3</sub> O <sub>4</sub>  VO/CF <sup>[25]</sup>	1.47	1 M KOH
Co <sub>3</sub> O <sub>4</sub> @NiPx/GC <sup>[26]</sup>	1.51	1 M KOH
Fe, P-NiCo <sub>2</sub> S <sub>4</sub> /NF <sup>[27]</sup>	1.55	1 M KOH
Co <sub>3</sub> O <sub>4</sub> /NF-Ar/O <sub>2</sub> <sup>[28]</sup>	1.56	1 M KOH

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