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## **Supporting Information**

# Prussian Blue Analog-Derived 2D Ultrathin CoFe<sub>2</sub>O<sub>4</sub> Nanosheets as High-activity Electrocatalysts for Oxygen Evolution Reaction in Alkaline and Neutral Mediums

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#### **Experimental Section**

## **Materials preparation**

**Preparation of CoFe<sub>2</sub>O<sub>4</sub> NSs:** First, 0.001 M potassium cobalticyanide (K<sub>3</sub>[Co(CN)<sub>6</sub>]) and 0.4 g polyvinylpyrrolidone (PVP) were dissolved into 10 ml DI water and form a transparent solution. Then, 0.0015 M cobalt (II) acetate tetrahydrate (Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O) was slowly added into the solution with stirring, and the mixture turned to pink when aged at room temperature. After stirring for 6 h, 0.001 M ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) was dropped in with stirring for another 6 h. Then, 3 M NaBH<sub>4</sub> was added in the solution until no gas produced. Finally, the power was separated by centrifugation, washed consecutively with water and ethanol and dried at 60°C in vacuum for 12 h. The preparation of FeCo<sub>2</sub>O<sub>4</sub>, NiCo<sub>2</sub>O<sub>4</sub>, CoNi<sub>2</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub> and FeNi<sub>2</sub>O<sub>4</sub> nanosheets were used the same strategy.

**Preparation of CoFe<sub>2</sub>O<sub>4</sub> NPs:** First, 0.001 M potassium cobalticyanide (K<sub>3</sub>[Co(CN)<sub>6</sub>]) and 0.4 g polyvinylpyrrolidone (PVP) were dissolved into 10 ml DI water and form a transparent solution. Then, 0.0015 M cobalt (II) acetate tetrahydrate (Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O) was slowly added into the solution with stirring, and the mixture turned to pink when aged at room temperature. After stirring for 6 h, 0.001 M ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) was dropped in with stirring for another 6 h. Then, Then 5.0 mL N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O was added into the above solution and transfer to the Teflon reactor with temperature of 180°C for 2 h. Finally, the power was separated by centrifugation, washed consecutively with water and ethanol and dried at 60°C in vacuum for 12 h.

## **Material characterizations**

Structural information and property of the catalysts were obtained by scanning electron microscopy (SEM; Hitachi S-4800), transmission electron microscope with energy dispersive X-ray (TEM; JEOL JEM-2100F, aberration-corrected STEM-EDX; Hitachi 2700C), powder X-ray diffraction (XRD; Bruker D8 Advance), X-ray photoelectron spectroscopy (XPS; HP 5950A ESCA), atomic force microscope (AFM; Bruker Dimension Icon), N<sub>2</sub> sorption was performed at 77 K on a Micromeritics ASAP 2020 to determine the specific surface area.

## **Electrochemical measurements**

Alkaline Medium: The oxygen evolution reaction (OER) activity was evaluated in a three-electrode configuration using a rotating disk electrode (RDE, ALS, Japan) at a rotation speed of 1,600 rpm in 1 M KOH (pH=13.7) aqueous solution at 25°C with a CHI 760E electrochemical workstation. A glassy carbon (GC) disk electrode (3 mm in diameter) used as the working electrode, carbon electrode and saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. 2.5 mg catalyst was weighted and mixed with 50  $\mu$ l Nafion solution (Aldrich, 5%) and 450  $\mu$ l DI water. The working electrode coated with 5  $\mu$ l ink, and dried naturally. All potentials were been converted to the reversible

hydrogen electrode (RHE) to unequivocally compensate for the pH changes, where  $E_{RHE} = E_{SCE} + 0.242 \text{ V} + 0.0591 \times \text{pH}$ . The overpotential ( $\eta$ ) was calculated according to the following formula:  $\eta = E_{RHE} - 1.23 \text{ V}$ . Linear sweep voltammetry (LSV) was recorded in 1.0 M KOH solution at a scan rate of 5 mV s<sup>-1</sup> to obtain the polarization curves. The long-time running tests used the carbon paper as the substrate. In all LSV curves, iR drop was compensated at 95% through the positive feedback model using the CHI 760E electrochemical analyzer.

**Neutral Medium:** For the OER in neutral medium, the oxygen evolution reaction (OER) activity was evaluated in a three-electrode configuration using a rotating disk electrode (RDE, ALS, Japan) at a rotation speed of 1,600 rpm in 0.2 M PBS (pH=7.0) at 25°C with a CHI 760E electrochemical workstation. LSV was recorded in 0.2 M PBS at a scan rate of 5 mV s<sup>-1</sup> to obtain the polarization curves. The iR drop was compensated at 95% through the positive feedback model using the CHI 760E electrochemical analyzer. The turnover frequency (TOF) was evaluated by the following standard equation: TOF=J\*A/(4\*F\*m). Here, J is the current density (A cm<sup>-2</sup>) at an overpotential of 350 mV. F is the Faraday constant (96,485 C mol<sup>-1</sup>). A and m are the area of the electrode and the number of moles of the active materials that were deposited onto the electrode, respectively. The mechanism of OER was studied by a rotating ring-disk electrode (RRDE-3A, ALS). Firstly, the content of the formed HO<sub>2</sub><sup>-</sup> was tested by fixing the ring potential at 1.5 V vs. RHE in O<sub>2</sub>-saturated 1 M KOH solution and collecting the ring current at a scan rate of 2 mV s<sup>-1</sup> under a rotation rate of 1,600 rpm. The Faradaic efficiency ( $\epsilon$ ) was determined by collecting the ring current when fixing the disk current at 200 µA and ring potential at 0.4 V vs. RHE in N<sub>2</sub>- saturated 1 M KOH solution. The Faradaic efficiency was calculated by the equation followed:  $\epsilon = I_r/(I_d*N)$ . Where I<sub>r</sub> is the collected ring current, I<sub>d</sub> is the disk current of 200 µA, N is the current collection efficiency (0.21 in this study).

**The rechargeable Zn-air batteries:** Zinc plate was used as the anode, 6 M KOH electrolyte was filled between the cathode and anode, and hydrophobic carbon paper was used as a current collector. The air cathodes were prepared by coating the catalysts (1.0 mg cm<sup>-2</sup>) on a hydrophobic carbon paper. The electrochemical measurements for rechargeable Zn-air batteries also conducted on a standard three-electrode system on CHI 760E electrochemical workstation.

## **DFT calculations**

DFT calculations were performed by using the Vienna Ab-initio Simulation Package (VASP). The interactions between ion cores and valence electrons were described by the Blöchl's all-electron-like projector augmented wave (PAW) method. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was adopted for the exchange-correlation interaction. The electron occupancies were determined according to the Fermi scheme with the energy smearing of 0.1 eV. The electron wave functions were expanded using the plane waves with a cutoff energy of 400 eV. The

geometries were optimized until the energy and the force were converged to  $1.0 \times 10^{-5}$  eV/atom and 0.01 eV/Å, respectively. The Brillouin zone integration was approximated by a sum over special selected k-point grid in reciprocal space using the  $3 \times 3 \times 1$  Monkhorst–Pack method during the geometry optimization. A semiempirical DFT-D2 force-field approach was employe to consider the influence of van der Waals (vdW) interaction in our calculations. Here, (111), (311) and (331) facets of CoFe<sub>2</sub>O<sub>4</sub> NS were chosen in our model. During the geometry optimizations, the model was fully relaxed. A vacuum layer as large as 15 Å between repeated slabs was used along the c direction normal to the catalyst surface to avoid periodic interactions.

The change of Gibbs free energy ( $\Delta$ Gi) for OER steps (1 and 3) in this work was calculated by:

$$\Delta G_i = \Delta E_i + \Delta ZPE_i - T\Delta S_i - \Delta G_{pH} + 1/2 G_{H2} - G_{H2O} - eU$$
(1)

The change of Gibbs free energy ( $\Delta$ Gi) for OER steps (2 and 4) in this work was calculated by:

$$\Delta G_i = \Delta E_i + \Delta ZPE_i - T\Delta S_i - \Delta G_{pH} + 1/2 G_{H2} - eU$$
<sup>(2)</sup>

The change of Gibbs free energy ( $\Delta$ Gi) for OER steps (5) in this work was calculated by:

$$\Delta G_i = \Delta E_i + \Delta ZPE_i - T\Delta S_i + G_{O2}$$
(3)

The reaction energy ( $\Delta E$ ) is obtained by calculating the DFT total energies. The harmonic vibrational frequency calculations were performed to determine the zero point energy ( $\Delta ZPE$ ).  $\Delta S$  is the change in entropy and T is room temperature (298.15 K). e is the transferred electron. U is the electrode potential with respect to the standard hydrogen electrode (defined at pH=0), and it is converted to the reversible hydrogen electrode (RHE) by subtracting kT×pH×ln10, the value of pH was assumed to be 14 in this work. Gas phase H<sub>2</sub>O at 0.035 bar is used as the reference state, where the gas phase H<sub>2</sub>O is in equilibrium with the liquid H<sub>2</sub>O at 298.15 K. The free energy of (e<sup>-</sup>-OH<sup>-</sup>) was computed assuming e<sup>-</sup>-OH<sup>-</sup>=1/2 G<sub>H2</sub>-G<sub>H2O</sub>-eU, where G<sub>H2</sub> and G<sub>H2O</sub> are the free energy of H<sub>2</sub> and H<sub>2</sub>O molecule. The free energy of O<sub>2</sub> (g) is obtained according to the free energy change of the reaction G<sub>O2</sub>=2G<sub>H2</sub>-2G<sub>H2</sub>+4.92. The entropies of the free molecules (such as H<sub>2</sub> and H<sub>2</sub>O) are taken from the NIST database, while the entropies of the other OER intermediates are calculated from the vibrational frequencies.

Fe-doped Co<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub>



Scheme S1 Schematic of  $CoFe_2O_4$  NS synthesis process.



Fig. S1 TEM images of (a)  $Co_3[Co(CN)_6]_2$  and (b) Fe-doped  $Co_3[Co(CN)_6]_2$  PBAs.



**Fig. S2** (a) Pictures from left to right: CoFe<sub>2</sub>O<sub>4</sub>, Co<sub>2</sub>FeO<sub>4</sub>, NiCo<sub>2</sub>O<sub>4</sub>, Ni<sub>2</sub>CoO<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub> and Ni<sub>2</sub>FeO<sub>4</sub>. (b) Pictures from left to right: CoFe<sub>2</sub>O<sub>4</sub>, Co<sub>2</sub>FeO<sub>4</sub>, NiCo<sub>2</sub>O<sub>4</sub>, Ni<sub>2</sub>CoO<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub> and Ni<sub>2</sub>FeO<sub>4</sub> after adding NaBH<sub>4</sub>.



**Fig. S3** LSV polarization curves of  $CoFe_2O_4$ ,  $FeCo_2O_4$ ,  $NiCo_2O_4$ ,  $CoNi_2O_4$ ,  $NiFe_2O_4$  and  $FeNi_2O_4$  nanosheets at a scan rate of 5 mV/s with a rotatin speed of 1,600 rpm.



Fig. S4 (a), (b) SEM images of  $CoFe_2O_4$  NSs (powder form); (c), (d) SEM images of  $CoFe_2O_4$  NSs (dispersed nanosheets, sonicated for 30 mins in ethanol).



Fig. S5 (a), (b) and (c) TEM images of CoFe<sub>2</sub>O<sub>4</sub> NSs. (d) HRTEM images of CoFe<sub>2</sub>O<sub>4</sub> NSs.



Fig. S6 (a) and (b) SEM images of CoFe<sub>2</sub>O<sub>4</sub> NPs.



**Fig. S7** (a) TEM; (b) HRTEM; (c) STEM-HAADF and the corresponding EDX mappings of  $CoFe_2O_4$  NPs. The image insert in (b) was the corresponding SAED patterns.



Fig. S8 EDX patterns of (a) CoFe<sub>2</sub>O<sub>4</sub> NSs and (b) CoFe<sub>2</sub>O<sub>4</sub> NPs.



**Fig. S9** XRD patterns of  $CoFe_2O_4$  NSs and  $CoFe_2O_4$  NPs. The XRD patterns of  $CoFe_2O_4$  NSs show no well-defined diffraction peaks, which was also reported in previous work.<sup>1, 14, 18</sup> It could be attributed to the fact that the ultrathin thickness of plates cannot satisfy the conditions of X-ray diffraction. On the contrary, the XRD patterns of  $CoFe_2O_4$  NPs show sharp peaks, which are the diffraction peaks of  $CoFe_2O_4$ . The results of XRD are in consistent with those of HRTEM and SAED tests.



**Fig. S10** (a) The N<sub>2</sub> adsorption-desorption isotherms, (b) pore size distribution of  $CoFe_2O_4$  NSs and  $CoFe_2O_4$  NPs. Based on the Brunauer-Emmett-Telle (BET) tests, the obtained specific surface area of  $CoFe_2O_4$  NSs and  $CoFe_2O_4$  NPs are 167.2 and 55.6 m<sup>2</sup>/g, respectively. The corresponding pore diameters of  $CoFe_2O_4$  NSs and  $CoFe_2O_4$  NPs are 3.52, and 3.61 nm, respectively. The nanosheet structure of the catalysts had a higher specific surface area, which can provide more active sites for OER.



**Fig. S11** LSV polarization curves of  $CoFe_2O_4$  NSs with or without iR-corrected at a scanning rate of 5 mV/s with a rotating speed of 1,600 rpm. It had been reported that the uncompensated resistance can vary during an experiment, and may even become a function of the current. Similarly, the resistance of uncompensated can increase in dilute solutions as the diffusion limiting current is approached, due to depletion of charge carriers.<sup>2</sup>



Fig. S12 LSV polarization curves of  $CoFe_2O_4$  NSs,  $CoFe_2O_4$  NPs, and  $RuO_2$ . The potentials of the three catalysts at a current density of 100 mA cm<sup>-2</sup> prove that the  $CoFe_2O_4$  NSs has the highest catalytic performance.



Fig. S13 CV polarization curves of CoFe<sub>2</sub>O<sub>4</sub> NSs and CoFe<sub>2</sub>O<sub>4</sub> NPs.



**Fig. S14** Electrochemical surface area (ECSA) tests in 1 M KOH with different scanning rates. Cyclic voltammetry curves of (a)  $CoFe_2O_4$  NSs and (c)  $CoFe_2O_4$  NPs with different scanning rates. The capacitive current measured at 1.38 V vs RHE was plotted as a function of scanning rates for (b)  $CoFe_2O_4$  NSs and (d)  $CoFe_2O_4$  NPs. The ECSAs of  $CoFe_2O_4$  NSs and  $CoFe_2O_4$  NPs were represented by the electrochemical double-layer capacitance ( $C_{dl}$ ), which is calculated by the scanning-rate-dependent CV curves at the potential range of 1.3-1.4 V. The  $C_{dl}$  of  $CoFe_2O_4$  NSs (49.3 mF cm<sup>-2</sup>) is higher than that of the  $CoFe_2O_4$ 

NPs (11.1 mF cm<sup>-2</sup>), which could be attributed to the enriched large number of oxygen vacancies and active sites of the nanosheet structure.



Fig. S15 Catalytic performance of OER with CoFe<sub>2</sub>O<sub>4</sub> NSs and CoFe<sub>2</sub>O<sub>4</sub> NPs after ECSA normalization.



**Fig. S16** (a) Ring current of  $CoFe_2O_4$  NSs catalyst on an RRDE (1,600 rpm) with a ring potential of 1.5 V vs RHE in O<sub>2</sub>-saturated 1 M KOH solution. (b) Ring current of  $CoFe_2O_4$  NSs catalyst on an RRDE (1,600 rpm) with a ring potential of 0.4 V vs RHE in Ar-saturated 1 M KOH solution.



Fig. S17 LSV polarization curves of CoFe<sub>2</sub>O<sub>4</sub> NSs before and after i-t test.



**Fig. S18** (a) The discharge and charge polarization curves and (b) Cycling curves of rechargeable Zn-air batteries based on  $CoFe_2O_4$  NSs and  $CoFe_2O_4$  NPs composite at a current density of 10 mA cm<sup>-2</sup>. The discharge polarization curves of  $CoFe_2O_4$  NSs and  $CoFe_2O_4$  NPs were obtained with a scanning current density of 100 mA cm<sup>-2</sup>. Figure S18(b) displays the charge–discharge cycling stability of the Zn-air battery at an current density of 10 mA cm<sup>-2</sup>. Apparently,  $CoFe_2O_4$  NSs exhibit lower charge potential and higher discharge potential than  $CoFe_2O_4$  NPs. The charge potential of  $CoFe_2O_4$  NSs only increased 0.01 V after 100 cycles testing, while  $CoFe_2O_4$  NPs increased 0.12 V. The discharge potential of  $CoFe_2O_4$  NSs only decreased 0.03 V after 100 cycles testing, while  $CoFe_2O_4$  NPs decreased 0.06 V.



**Fig. S19** Polarization curves of  $CoFe_2O_4$  NSs and  $CoFe_2O_4$  NPs with a sweeping rate of 5 mV/s and a rotating speed of 1,600 rpm without iR-corrected in neutral medium.



Fig. S20 Post SEM image of CoFe<sub>2</sub>O<sub>4</sub> NSs after i-t test.



**Fig. S21** Post (a) TEM, (b) and (c) HRTEM, (d) HAADF-STEM images and EDX mappings of  $CoFe_2O_4$  NSs. The carbon in the catalyst could be attributed to the carbon paper.



**Fig. S22** XPS analysis of full spectra (a), O (b), Co (c) and Fe (d) for  $CoFe_2O_4$  NSs before and after long-time running tests.



Fig. S23 OER mechanism and elementary step catalyzed by CoFe<sub>2</sub>O<sub>4</sub> NSs.

In alkaline solution, the OER steps are considered as follows:

$$e^{+} + OH^{-} \rightarrow *OH^{+} e^{-}$$
 (1)

$$*OH + OH^{-} \rightarrow *O + H_2O + e^{-}$$
<sup>(2)</sup>

$$*O + OH^{-} \rightarrow *OOH + e^{-}$$
(3)

$$*OOH + OH^{-} \rightarrow *O_2 + H_2O + e^{-}$$
(4)

$$*O_2 \rightarrow *+O_2 \text{ (gasform)}$$
 (5)

For OER, the first step was the adsorption and discharge of  $OH^-$  at the catalyst surface (denoted as \*) and to form the adsorbed \*OH species. The second step was the reaction of adsorbed \*OH with the  $OH^-$  to form the adsorbed \*O species and release a H<sub>2</sub>O molecule and an electron. The third step was the reaction of the adsorbed \*O with  $OH^-$  to form the adsorbed \*OOH species and an electron. The fourth step was the reaction of the  $OH^-$  with \*OOH to form \*O<sub>2</sub>, accompanied by the release of a H<sub>2</sub>O molecule and an electron. The last step was the release of \*O<sub>2</sub> from the catalyst surface.<sup>27</sup>



Fig. S24 An optical image of  $CoFe_2O_4$  NSs operating at 10 mA cm<sup>-2</sup> with generated oxygen bubbles on the electrode surface.

Catalysts	Overpotential@10 mA cm <sup>-2</sup> (mV)	Tafel slope (mV dec <sup>-1</sup> )	Electrolyte	Substrate	Reference
CoFe <sub>2</sub> O <sub>4</sub> NSs CoFe <sub>2</sub> O <sub>4</sub> NPs RuO <sub>2</sub>	275 339 325	42.1 44.2 79.1	1 M KOH 1 M KOH 1 M KOH	GCE GCE GCE	This work This work This work
CoFe <sub>2</sub> O <sub>4</sub> /C powders	310	61	1 M KOH	NF@NC	3
CoFe <sub>2</sub> O <sub>4</sub> /PANI MWCNTs	310	30.69	1 M KOH	GCE	4
Amorphous CoFe <sub>2</sub> Ox	510	48	0.1 M KOH	GCE	5
Crystalline CoFe <sub>2</sub> O <sub>4</sub>	570	61	0.1 M KOH	GCE	3
Co-Fe-O/rGO	340	31	1 M KOH	GCE	6
ESM/CNTG/ NiCo <sub>2</sub> O <sub>4</sub>	370	158	1 M KOH	Eggshell membrane	7
Co <sub>3</sub> O <sub>4</sub> /NiCo <sub>2</sub> O <sub>4</sub> Nanocages	340	88	1 M KOH	NF	8
NixCo3-xO4	330	60	1 M NaOH	Ti foam	9
Co-Bi NS/G nanosheet	290	53	1 M KOH	GCE	10
Ni-Co oxides layers	325	39	1 M NaOH	Au coating microscope slides	11
CoMn-LDH	325	43	1 M KOH	GCE	12
Co <sub>3</sub> O <sub>4</sub> /Co-Fe oxide DSNBs	297	61	1 M KOH	GCE	13
Co-UNMs	307	76	1 M KOH	GCE	14
CoPt@Co(OH) <sub>2</sub> nanosheets	387	120	1 M KOH	Carbon cloth	15
CoS nanosheets	361	64	1 M KOH	Ti mesh	16
Co-B nanosheet	520	108	0.1 M KOH	Ti mesh	17
Fe-Co oxide nanosheets	308	36.8	0.1 M KOH	GCE	18

 Table S1. Comparison of OER catalytic performance of noble metal-free catalysts in alkaline condition.

Catalysts	Onset Potential (V vs. RHE)	j at 1.8 V (mA cm-2)	Reference
CoFe2O4 NSs	1.5	4.8	This work
CoFe2O4 NPs	1.7	1.0	This work
Co3S4 ultrathin nanosheet	1.53	2.4	19
Co(OH)2	1.61	0.57	20
Co0.9Ni0.1NCN	1.6	3	21
A-CoS4.6O0.6 PNCs	1.5	4.8	22
Au-Co(OH)2	1.51	1.6	23
Mn2O3	1.71	0.025	24
Co3O4/SWNTS	1.7	6	25
Co-Bi NS	1.6	5.3	10
Fe-based film	1.7	5.1	26

 Table S2 Comparison of OER catalytic performance of noble metal-free catalysts in neutral solution.

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