# **Electronic Supplementary Information**

# Atomic-level Orbital Coupling in Tri-metal Alloy Site Enables Highlyefficient Reversible Oxygen Electrocatalysis

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#### **Experimental section:**

**Materials:** cetyltrimethylammonium bromide, nickel (II) nitrate hexahydrate, zinc(II) nitrate hexahydrate, zinc(II) nitrate hexahydrate, zinc(II) nitrate hexahydrate, iron nitrate, iron acetate, polyvineypirrolydone (PVP, K30), N,N-Dimethylformamide (DMF) and methanol were purchased from Sigma-Aldrich. All reagents were of analytical grade and used as received.

#### Materials characterizations:

The composition and crystalline phase of the sample were investigated with powder X-ray diffraction measurements (XRD, Shimadzu XRD-6000, Japan), energy dispersive spectrometry (EDS, Hitachi S-4800, and JEM-2100, Japan), X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy (XPS and UPS, Thermo ESCALAB 250XI, America). The morphology and microstructure of the product were observed with a scanning electron microscope (SEM, Hitachi S-4800, Japan) and a high-resolution transmission electron microscope (TEM, JEM-2100, Japan). Raman spectra were recorded at room temperature in the spectral range of 1000-2200 cm<sup>-1</sup> using a Raman spectromicroscopy (LabRAM HR800, Horiba Jobin Yvon, France). FT-IR spectra were recorded for KBr-diluted samples using a Nicolet Magna 750 IR spectrometer at wavenumbers of 1000-1500 cm<sup>-1</sup>.

## **Electrochemical characterizations:**

The measurement of ORR and Zn-air battery: Each catalyst (10 mg) was dispersed into a solution (1.92 mL) containing ethanol/H<sub>2</sub>O (1/1, v/v) and Nafion (5 wt%, 80  $\mu$ L) by ultrasonication for 30 min for the following procedures. The ORR performances were evaluated on a CHI760D electrochemical analyzer using a standard three-electrode system. The glass carbon electrode after loading the catalyst was used as the working electrode. A carbon rod was used as the counter

electrode for ORR tests. A saturated calomel electrode (SCE) was selected as the reference electrode. For ORR measurements, the dispersion (10  $\mu$ L) was uniformly dropped onto a freshly polished glassy carbon electrode (4 mm in diameter), which was dried under ambient conditions. The electrochemical experiments were carried out in an O<sub>2</sub>-saturated 0.1 M KOH electrolyte for the ORR. The potential cycling was repeated until the reproducible CV curves were obtained before the measurements. All current densities were normalized to the geometrical surface area and the measured potential *vs*. SCE was converted to the potential *vs*. the reversible hydrogen electrode (RHE). Rotating ring disk electrode (RRDE) (*ca*. 0.1256 cm<sup>2</sup> for disk and *ca*. 0.0707 cm<sup>2</sup> for the ring) measurements were carried out at 1600 rpm. The electron transfer number (*n*) could also be determined from RRDE measurements on the basis of the disk current (I<sub>d</sub>) and ring current (I<sub>r</sub>) *via* the following equation (1):

$$n = 4 \times I_d / (I_d + I_r / N) \tag{1}$$

The peroxide percentage (%  $HO_2^-$ ) was calculated based on equation (2):

Where N is the current collection efficiency of the Pt ring, 0.37.

Ni foams were carefully washed with HCl (1 M) and then rinsed with absolute ethanol and distilled water to remove any oxides on the surface. The catalyst (10 mg) was dispersed into a solution (1.92 mL) containing ethanol/H<sub>2</sub>O (1/1, v/v) and Nafion (5 wt%, 80  $\mu$ L) by ultrasonication for the following procedures. The resultant inks were carefully dropped onto the respective Ni foams and then kept in a vacuum container for 30 min. For the primary Zn-air battery, the loading amounts of the catalyst and Pt/C were 1 mg/cm<sup>2</sup>, respectively. For the rechargeable Zn-air battery, the loading amount of the catalyst was 1 mg/cm<sup>2</sup>, while the Pt/C and RuO<sub>2</sub> inks were mixed with a ratio of 1:3,

and a total catalyst loading amount of 1 mg/cm<sup>2</sup> was obtained. The Zn-air battery was assembled with Zn powder, a 6 M KOH solution [mixed with 0.2 M Zn(Ac)<sub>2</sub> for rechargeable Zn-air battery], and an air cathode comprising a catalyst layer and gas-diffusion layer was used as a backing layer next to the Ni foam-based catalyst layer to prevent electrolyte leakage.

The measurement of OER: The OER activity of the product was characterized on a CHI760D electrochemical workstation with a typical 3-electrode setup. The working electrode was prepared using the as-prepared powders (85 wt%) as the active material and polyvinylidene fluoride (15 wt%) as the binder. They were mixed in N-methylpyrrolidone (NMP) to form a sample suspension. The working electrode was fabricated by drop-casting the sample suspension, sonicated for 30 min before use, onto a graphite electrode (1 cm × 1 cm), and dried at 80 °C in an oven. The mass loading of the active material on the working electrode was controlled to be around 0.5 mg/cm<sup>2</sup>. A platinum foil counter electrode and a Hg/HgO reference electrode were employed to complete the 3-electrode setup. For the measurements, 1 M KOH (pH = 13.85) aqueous solution was used as the electrolyte. The potential values for the OER in this study were converted and referred to the reversible hydrogen electrode (RHE) using the Nernst equation:  $E_{RHE} = E_{Hg/HgO} + 0.059 \text{pH}$ , where E<sub>Hg/HgO</sub> is the experimentally measured potential against the Hg/HgO reference electrode. All linear scan voltammetry (LSV) polarization curves were *iR*-corrected with respect to the involved solution resistances. The over-potential ( $\eta$ ) was calculated using the equation:  $\eta = E_{RHE} - 1.23$ . Prior to electrochemical measurements, the working electrode was conditioned by cycling through the potential window of 0 to 0.8 V vs. Hg/HgO thirty times at a scan rate of 100 mV/s. The polarization curves were recorded with a linear potential sweep at a scan rate of 2 mV/s. The electrochemical impedance spectroscopy (EIS) was conducted in the frequency range of  $10^5$  to 0.01 Hz with an AC amplitude of 5 mV and the applied potential set at  $E_{Hg/HgO} = 0.6$  V. The electrochemical active surface area (ECSA) of the catalysts was characterized from the double-layer charging curves obtained from cyclic voltammetry at increasing scan rates within a non-Faradaic potential window (0.895-0.995 V *vs.* RHE), in which no Faradaic redox reactions occur. A long-term stability test was carried out with chronopotentiometric measurements. For calculation of the turnover frequency (TOF), reductive negative scan peak areas were firstly determined from cyclic voltammograms recorded at a specific scan rate, for example, 300 mV/s. Charge (Q) can be obtained with the formula: Q = peak area/300 mV/s. Assuming a single-electron transfer reaction in the reduction process, the number of surface active sites (n) can be calculated with the equation: n =  $Q/(1\times1.602\times10^{-19})$ . Finally, TOF values are obtained from TOF =  $j\times N_A/(4\times n\times F)$  (j = current density,  $N_A$  = Avogadro number, F = Faraday constant). The work function (W<sub>F</sub>) could be obtained with the formula: W<sub>F</sub> =  $hv - (E_{cutoff} - E_F)$ , where, hv represented the energy of the incident photon (21.22 eV),  $E_{cutoff}$  was the onset level connected with the secondary edge,  $E_F$  was the Fermi level ( $E_F$ , set to 0 eV). W<sub>F</sub> reflected the dynamics of electrons on the surface of the samples.

**Computation method:** Spin-polarization density functional theory (DFT) + U calculations were carried out by using the projector augmented wave (PAW) method as implemented in the Vienna *ab Initio* Simulation Package.<sup>[1]</sup> The Perdew-Burke-Ernzerhof functional for the exchange-correlation term was used for all calculations. The energy cutoff for plane-wave expansion of the PAWs is 450 eV. Calculations reached convergence until the energy and force dropped below 10<sup>-4</sup> eV and 0.05 eV/Å, respectively. According to the previous report, the Fe-Co-Ni model of graphene interacting with the Fe-Co-Ni (111) surface was obtained simply by adding layer of graphene on top of the Fe-Co-Ni (111) surface.<sup>[2]</sup> Similarly, the Co-Ni@NDC and Fe-Co@NDC models were

also constructed by similar method. In the vertical direction, a vacuum layer of about 20 Å in thickness was introduced to avoid the interaction between neighboring image structures. In order to precisely reflect the strong-correlation of d electrons in Fe, Co and Ni atom, the values of U-J parameters for Fe, Co and Ni is set as 3.29, 3.42 and 3.4 eV, respectively.<sup>[3]</sup> The 2×2×1 and 5×2×1 k-points sampling with the Monkhorst-Pack method was used for structure optimization and surface calculations, respectively. To better describe the interaction between active intermediates and catalysts, Grimme's method (DFT-D3) was employed in the surface adsorption calculations. Finally, the adsorption energies ( $E_{ads}$ ) were calculated as:  $E_{ads} = E_{ad/sub} - E_{ad} - E_{sub}$ , where  $E_{ad/sub}$ ,  $E_{ad}$ , and E<sub>sub</sub> were the optimized adsorbate/substrate system, the adsorbate in the structure and the clean substrate, respectively. The free energy was calculated as follows:  $G = E_{elec}$  -  $E_{ZPE}$  - TS, where G, Eelec, EZPE, and TS (300 K) were the free energy, total energy from DFT calculations, zero-point energy, and entropic contributions, respectively. The free energy for \*OH, \*O, and \*OOH was obtained according to the formula:  $\Delta G = eU + \Delta E_{ZPE} + \Delta E - T\Delta S$ , where U stands for applied potential in the calculation,  $\Delta E_{ZPE}$ ,  $\Delta E$ , T, and  $\Delta S$  are the zero-point energy, the binding energy of the intermediates (\*OH, \*O, and \*OOH), temperature (298.15 K), and entropy changes, respectively. Moreover, the equilibrium potential is 1.23 eV at room temperature. Therefore, the overpotential of OER is determined by following equations:  $\eta_{OER} = U_{OER} - 1.23$ ;  $U_{OER} = Max(\Delta G_{*OH}, \Delta G_{*O} - \Delta G_{*OH}, \Delta G_{*OH})$  $\Delta G_{*OOH}$  -  $\Delta G_{*O}$ , 4.92 eV -  $\Delta G_{*OOH}$ /e. The overpotential of ORR is expressed as follows:  $\eta_{ORR}$  = 1.23 - U<sub>ORR</sub>; U<sub>ORR</sub> = -Max ( $\Delta G_{*OOH}$  - 4.92 eV,  $\Delta G_{*O}$  -  $\Delta_{G^{*OOH}}$ ,  $\Delta G_{*OH}$  -  $\Delta G_{*O}$ ,  $\Delta G_{*OH}$ )/e.



Figure S1 (a) XRD pattern of Zn/Ni-ZIF-8 nanocubes together with a simulated pattern for ZIF-8;

(b) EDS spectrum and (c-d) SEM images of Zn/Ni-ZIF-8 nanocubes.



Figure S2 (a-b) SEM and (c) TEM images, (d) XRD pattern, as well as (e) EDS elemental mapping

images of Zn/Ni-ZIF-8@Fe/Co-ZIF-9 nanostructures.



Figure S3 Photographs of (a) Zn/Ni-ZIF-8 nanocubes, (b) Fe/Co-ZIF-9 nanocubes and (c) Zn/Ni-

ZIF-8@Fe/Co-ZIF-9 nanostructures.



Figure S4 FT-IR spectra of Zn/Ni-ZIF-8 nanocubes, Fe/Co-ZIF-9 nanocubes and Zn/Ni-ZIF-

8@Fe/Co-ZIF-9 nanostructures.



Figure S5 Raman spectrum of Fe-Co-Ni@NDC nanobox.



Figure S6 (a-b) XRD pattern, (c-d) SEM images, (e) EDS spectrum and (f-h) XPS spectra of

Ni@NDC product.



Figure S7 (a) XRD pattern of Fe/Co-ZIF-9 nanocubes together with simulated pattern for ZIF-9;

(b) EDS spectrum and (c-d) SEM images of Fe/Co-ZIF-9 nanocubes.



Figure S8 (a-b) XRD pattern, (c) EDS spectrum, (d-e) SEM images and (f-i) XPS spectra of Fe-

Co@NDC product.



Figure S9 (a) XRD pattern, (b-c) SEM and (d) TEM images, as well as (e) EDS elemental mapping

images of Zn/Ni-ZIF-8@Co-ZIF-9 nanostructures.



Figure S10 (a-b) XRD pattern, (c-d) SEM images and (e-h) XPS spectra of Co-Ni@NDC product.



Figure S11 (a) XRD pattern, (b) EDS spectrum and (c-d) SEM images of Zn-ZIF-8 nanocubes; (e)

XRD pattern, (f-g) SEM and (h-i) TEM images of NDC product.



Figure 12 (a) Working functions and (b) valence band maximum values of the as-prepared catalysts.Notes: (tomato red) Fe-Co-Ni@NDC, (dark gold-orange) Co-Ni@NDC and (royal blue) Ni@NDC.



**Figure S13** (a) Methanol crossover tolerance for ORR and (b) durability evaluation on i-t chronoamperometric responses using different catalysts (0.89 V); (c) LSV curves of Fe-Co-Ni@NDC sample before (tomato red) and after (gray) 22 h operating. Notes: (red) Fe-Co-Ni@NDC, and (black) Pt/C.



Figure S14 Reduction peaks recorded at 300 mV/s for determination of numbers of surface-active

sites: (a) Fe-Co-Ni@NDC, (b) Fe-Co@NDC, (c) Co-Ni@NDC, (d) Ni@NDC and (e) NDC.



**Figure S15** Cyclic voltammograms recorded at increasing scan rates for OER over in 1 M KOH: (a) Fe-Co-Ni@NDC, (b) Fe-Co@NDC, (c) Co-Ni@NDC, (d) Ni@NDC and (e) NDC; (f) linear fitting of current density difference (recorded at 0.945 V vs. RHE) vs. scan rate in 1.0 KOH to determine C<sub>dl</sub>.



Figure S16 Amounts of O2 experimentally measured and theoretically calculated versus time at the

current density of 10 mA/cm<sup>2</sup>.



Figure S17 XRD patterns (a-b), XPS spectra (c-e), SEM (f) and TEM images (g-i) of Fe-Co-Ni@NDC electrocatalyst after OER long-term stability measurement.



**Figure S18** The side view of (a) before and (b) after optimization of Co-Ni@NDC; the side view of (c) before and (d) after optimization of Fe-Co@NDC; the side view of (e) before and (f) after optimization of Fe-Co-Ni@NDC.



Figure S19 Charge density difference of (a) Co-Ni@NDC, (b) Fe-Co@NDC and (c) Fe-Co-Ni@NDC (Cyan and yellow regions represent the decreased and increased electron density, respectively).



Figure S20 Electron localization function (ELF) of (a) Co-Ni@NDC, (b) Fe-Co@NDC and (c)

Fe-Co-Ni@NDC.



Figure S21 Digital image of the Zn-air button battery.

Catalysts	E <sub>1/2</sub> vs RHE (V)	$j_{ m L}$	Tafel slope (mV/dec)
Fe-Co-Ni@NDC	0.902	5.36	72
Co-Ni@NDC	0.843	5.34	107
Ni@NDC	0.793	4.98	109
NDC	0.786	4.40	115
Fe-Co@NDC	0.846	2.75	125
Pt/C	0.833	5.31	89

Table S1 Summary of ORR performances in 0.1 M KOH of five catalysts and Pt/C.

Table S2 Summary of OER performances in 1 M KOH of five catalysts and RuO<sub>2</sub>.

Catalysts	η <sub>10</sub> (mV)	Tafel slope (mV/dec)	C <sub>dl</sub> (mF/cm²)	TOF (s <sup>-1</sup> )
Fe-Co-Ni@NDC	359	56	6.63	17.09
Fe-Co@NDC	381	84	5.36	7.18
Co-Ni@NDC	414	96	0.17	2.73
Ni@NDC	N/A	115	0.27	0.15
NDC	N/A	408	0.23	0.05
RuO <sub>2</sub>	302	72	N/A	N/A

Table S3 Comparison of ORR in 0.1 M KOH and OER performances in 1.0 M KOH: present wor	·k
vs. literature.	

Catalysts	$E_{1/2}$ (V) for ORR	$\eta_{10}(mV)$ for OER	Δ <i>E</i> (V)	References
Fe-Co-Ni@NDC	0.902	359	0.687	This work
FeCo/FeCoNi@NCNTs-	0.850	378	0.758	S4
HF				
Co/N-CNTs	0.840	390	0.780	S5
FeNO-CNT-CNFF	0.870	430	0.790	S6
FeCo-N-C-700	0.896	370	0.710	S7
Pd/FeCo	0.850	320	0.700	S8
1nm-CoO <sub>x</sub>	0.850	370	0.750	S9
CN@NC	0.830	400	0.800	S10
N-CoNi/PCS	0.800	540	0.970	S11
Fe <sub>1</sub> Co <sub>1</sub> -CNF	0.807	500	0.923	S12
FeNi@NCNT-CP	0.850	360	0.740	S13

Table S4 Comparison of the peak power density and capacity: present work vs. literature.

Catalysts	Current density (mA/cm²)	Peak power density (mW/cm²)	Capacity (mAh/g at 10 mA/cm²)	References
Fe-Co-Ni@NDC	397	247	894	This work
FeCo-N-C-700	240	150	518	S7
Pd/FeCo	280	117	821	S8
Ni-Fe-MoN NTs	315	118	753	S14
FeNC-S-Fe <sub>x</sub> C/Fe	N/A	149	663	S15

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