Electronic Supplementary Information

Open-mouth N-doped Carbon Nanoboxes Embedded with Mixed Metal Phosphide Nanoparticles as High-efficiency Catalysts for Electrolytic Water Splitting

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Experimental Section

Materials:

Nickel (II) sulfate hexahydrate (NiSO₄·6H₂O), potassium hexacyanoferrate (III) (K₃[Fe(CN)₆]), trisodium citrate dihydrate (Na₃C₆H₅O₇·2H₂O), nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O), potassium hexacyanocobaltate (III) (K₃[Co(CN)₆]), sodium hypophosphite (NaH₂PO₂), ethanol, and ammonium hydroxide were purchased from Sigma-Aldrich. All reagents were of analytical grade and used as received.

Materials preparation:

Preparation of $Ni_3[Fe(CN)_6]_2 \cdot H_2O$ *nanocubes*: Typically, 0.006 mol of NiSO₄·6H₂O and 0.0075 mol of Na₃C₆H₅O₇·2H₂O were dissolved in 590 mL of deionized water to form solution A. Then, 0.004 mol of K₃[Fe(CN)₆] was dissolved in 10 mL of deionized water to form solution B. Solutions A and B were thoroughly mixed under magnetic stirring for precipitation, followed by aging for 24 h. The precipitates were collected with a centrifuge, washed with deionized water and absolute ethanol five times, and then dried in vacuum at 50 °C for 24 h to afford the Ni₃[Fe(CN)₆]₂•H₂O nanocubes.

Preparation of $Ni_3[Fe(CN)_6]_2 \cdot H_2O$ *hollow nanocubes:* In a typical run, 100 mL of H₂O and 15 mL of NH₃·H₂O were added into 50 mL of ethanol and then 100 mg of Ni₃[Fe(CN)₆]₂•H₂O nanocube was introduced. The resulted suspension was stirred at room temperature for 20 min. After that, Ni₃[Fe(CN)₆]₂•H₂O hollow nanocubes were collected with a centrifuge, washed with deionized water and absolute ethanol five times, and then dried in vacuum at 70 °C overnight.

Preparation of Ni₃[Co(CN)₆]₂•12H₂O nanocubes: Typically, 0.006 mol of Ni(NO₃)₂·6H₂O and 0.009 mol of Na₃C₆H₅O₇·2H₂O were dissolved in 20 mL of deionized water to form solution A.

Then, 0.004 mol of $K_3[Co(CN)_6]$ was dissolved in 20 mL of deionized water to form solution B. Solutions A and B were thoroughly mixed under magnetic stirring for 5 min, followed by aging for 7 days. The precipitate was collected with a centrifuge, washed with deionized water and absolute ethanol five times, and then dried in vacuum at 70 °C for 24 h to afford the Ni₃[Co(CN)₆]₂•12H₂O nanocubes.

Preparation of $Ni_3[Co(CN)_6]_2 \cdot 12H_2O$ *hollow nanocubes*: In a typical run, 100 mL of H₂O and 15 mL of NH₃·H₂O were added into 50 mL of ethanol and then 100 mg of Ni₃[Co(CN)₆]₂ \cdot 12H₂O nanocubes were introduced. The resulted suspension was stirred at room temperature for 20 min. After that, Ni₃[Co(CN)₆]₂ · 12H₂O hollow nanocubes were collected with a centrifuge, washed with deionized water and absolute ethanol five times, and then dried in vacuum at 70 °C overnight.

Preparation of $Ni_3[Co(CN)_6]_2 \cdot 12H_2O$ *coated* $Ni_3[Fe(CN)_6]_2 \cdot H_2O$ *nanocubes: Typically*, 0.243 mol of Ni(NO₃)₂ · 6H₂O and 0.364 mol of Na₃C₆H₅O₇ · 2H₂O were dissolved in 8 mL of deionized water and then 100 mg of Ni₃[Fe(CN)₆]₂ • H₂O nanocubes were introduced. The resulted suspension was stirred at room temperature for 10 min to form solution A. Then, 0.162 mol of K₃[Co(CN)₆] was dissolved in 8 mL of deionized water to form solution B. Solutions A and B were thoroughly mixed under magnetic stirring for 2 h, followed by aging for 7 days. The precipitates were collected with a centrifuge, washed with deionized water and absolute ethanol five times, and then dried in vacuum at 60 °C for 24 h to afford the Ni₃[Co(CN)₆]₂ · 12H₂O coated Ni₃[Fe(CN)₆]₂·H₂O nanocubes.

Preparation of open-mouth $Ni_3[Co(CN)_6]_2 \cdot 12H_2O$ coated $Ni_3[Fe(CN)_6]_2 \cdot H_2O$ hollow nanocubes: Typically, 100 mL of H₂O and 15 mL of NH₃·H₂O were added into 50 mL of ethanol and then 100 mg of Ni₃[Co(CN)₆]₂•12H₂O coated Ni₃[Fe(CN)₆]₂•H₂O nanocubes were introduced. The resulted suspension was stirred at room temperature for 20 min. After that, open-mouth $Ni_3[Co(CN)_6]_2 \cdot 12H_2O$ coated $Ni_3[Fe(CN)_6]_2 \cdot H_2O$ hollow nanocubes was collected with a centrifuge, washed with deionized water and absolute ethanol five times, and then dried in vacuum at 70 °C overnight. For ammonia etching of $Ni_3[Fe(CN)_6]_2 \cdot H_2O$ or $Ni_3[Co(CN)_6]_2 \cdot 12H_2O$ nanocubes, the process was the same as above except that $Ni_3[Co(CN)_6]_2 \cdot 12H_2O$ coated $Ni_3[Fe(CN)_6]_2 \cdot H_2O$ nanocubes were replaced with the same amount of $Ni_3[Fe(CN)_6]_2 \cdot H_2O$ or $Ni_3[Co(CN)_6]_2 \cdot H_2O$ nanocubes.

Preparation of E-(Fe-Ni)P@CC/(Co-Ni)P@CC: Typically, 0.02 g of Ni₃[Co(CN)₆]₂•12H₂O coated Ni₃[Fe(CN)₆]₂•H₂O open-mouth hollow nanocubes and 0.2 g of NaH₂PO₂ were loaded separately into two porcelain boats, and the two precursor-containing boats were situated side by side at the center of a tube furnace with the NaH₂PO₂-containing boat being placed upstream. The calcination was conducted at 400 °C for 3 h with a heating rate of 5 °C/min under N₂ atmosphere, followed by cooling to ambient temperature under N₂ gas flow. For thermal phosphorization of other samples, the procedures are the same as above.

Materials Characterizations:

The composition and crystalline phase of the sample were investigated with powder X-ray diffraction measurements (XRD, Shimadzu XRD-6000, Japan), X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, America), and energy dispersive spectrometry (EDS, Hitachi S-4800 and JEM-2100, Japan). 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⁻¹ using a Raman spectromicroscope

(LabRAM HR800, Horiba Jobin Yvon, France).

Electrochemical characterizations:

The electrochemical performances of the samples were characterized on a CHI760D electrochemical workstation in a three-electrode system. 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 \times 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/cm². A platinum foil (for OER) or graphite electrode (for HER) was taken as the counter electrode and an Hg/HgO reference electrode were employed to complete the three-electrode system. For the measurements, 1 M KOH (pH = 13.9) aqueous solution was used as the electrolyte. Potentials reported in this study were converted to values referring to the reversible hydrogen electrode (RHE) using the equation $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.059$ pH, where $E_{Hg/HgO}$ is the applied potential against the Hg/HgO reference electrode. All the reported current densities were iR-compensated. The over-potential (η) was calculated using the following equations: $\eta_{\text{OER}} = E_{\text{RHE}}$ - 1.23 and $\eta_{\text{HER}} =$ E_{RHE} - 0. Prior to electrochemical measurements, the working electrode was conditioned by cycling through the potential window of 0 to 0.8 V (for OER) or -0.8 to -1.5 V (for HER) vs. Hg/HgO thirty times at a scan rate of 100 mV/s. The polarization curves for the OER and HER were recorded with a linear potential sweep at a scan rate of 2 mV/s. The electrochemical impedance spectroscopy measurements were conducted in the same set up from 10^5 to 0.01 Hz with an AC amplitude of 5 mV. Long-term stability test was carried out using chronopotentiometric

measurements. The electrochemical active surface area (ECSA) of the catalysts was measured from the double-layer charging curves using cyclic voltammetry at increasing scan rates within a small potential range (0.87-0.97 V vs. RHE) where no Faradaic redox reactions occur. The alkaline electrolyzer was constructed by using the same catalysts for the cathode and anode. The overall water splitting performance was evaluated using linear sweep voltammetry (LSV) in a two-electrode configuration in 1.0 M KOH. 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 one-electron transfer process for both reduction and oxidation, 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).



Fig. S1 XRD pattern of $Ni_3[Fe(CN)_6]_2 \cdot H_2O$ nanocubes together with standard card for $Ni_3[Fe(CN)_6]_2 \cdot H_2O$.



Fig. S2 (a)-(c) SEM images and (d) EDS spectrum of $Ni_3[Fe(CN)_6]_2 \cdot H_2O$ nanocubes.



Fig. S3 (a)-(c) SEM images and (d) EDS spectrum of $Ni_3[Co(CN)_6]_2 \cdot 12H_2O$ coated

 $Ni_3[Fe(CN)_6]_2 \bullet H_2O$ nanocubes.



Fig. S4 (a)-(b) TEM images of Ni₃[Co(CN)₆]₂•12H₂O coated Ni₃[Fe(CN)₆]₂•H₂O nanocubes.



Fig. S5 XRD pattern of $Ni_3[Co(CN)_6]_2 \cdot 12H_2O$ coated $Ni_3[Fe(CN)_6]_2 \cdot H_2O$ nanocubes together with XRD standard cards of $Ni_3[Co(CN)_6]_2 \cdot 12H_2O$ and $Ni_3[Fe(CN)_6]_2 \cdot H_2O$.



Fig. S6 (a) High-angle annular dark-field scanning transmission electron microscopy image and elemental mapping images of Ni₃[Co(CN)₆]₂•12H₂O coated Ni₃[Fe(CN)₆]₂•H₂O nanocubes: (b) Co, (c) Ni, (d) Fe, (e) C, and (f) N.



Fig. S7 TEM/EDS line scans of Ni₃[Co(CN)₆]₂•12H₂O coated Ni₃[Fe(CN)₆]₂•H₂O nanocubes: (a) signal collecting line, (b) Fe, (c) Co, and (d) Ni.



Fig. S8 (a)-(c) SEM images of open-mouth Ni₃[Co(CN)₆]₂•12H₂O coated Ni₃[Fe(CN)₆]₂•H₂O

nanoboxes.



Fig. S9 Raman spectrum of E-(Fe-Ni)P@CC/(Co-Ni)P@CC.



Fig. S10 (a) High-angle annular dark-field scanning transmission electron microscopy image and elemental mapping images of E-(Fe-Ni)P@CC/(Co-Ni)P@CC: (b) Co, (c) Ni, (d) Fe, (e) C, (f) N, and (g) P.



Fig. S11 (a)-(b) SEM, (c) TEM images, and (d) EDS spectrum of (Fe-Ni)P@CC/(Co-Ni)P@CC

nanocubes.



Fig. S12 XRD pattern of (Fe-Ni)P@CC derived from Ni_3 [Fe(CN)₆]₂•H₂O nanocubes together with



XRD standard cards of FeP (00-003-1066) and $\rm Ni_5P_4$ (00-018-0883).

Fig. S13 (a)-(c) SEM images and (d) EDS spectrum of (Fe-Ni)P@CC derived from Ni₃[Fe(CN)₆]₂•H₂O nanocubes.



Fig. S14 SEM images: (a)-(b) Ni₃[Fe(CN)₆]₂•H₂O hollow nanocubes and (c)-(d) E-(Fe-Ni)P@CC.

Fig. S12-S13 exhibit the XRD pattern, SEM images, and EDS spectrum of (Fe-Ni)P@CC. After thermal phosphorization, Ni₃[Fe(CN)₆]₂•H₂O nanocubes were converted to Ni₅P₄ (ICDD No. 00-018-0883) and FeP (ICDD No. 00-003-1066) nanoparticles embedded in N-doped C. If examined carefully, the discrete cube shape morphology of Ni₃[Fe(CN)₆]₂•H₂O changed significantly to aggregated nanoparticles. Similar phenomenon is observed for conversion of Ni₃[Fe(CN)₆]₂•H₂O hollow nanocubes to E-(Fe-Ni)P@CC as evident in Fig. S14.



Fig. S15 XRD pattern of Ni₃[Co(CN)₆]₂•12H₂O nanocubes and corresponding standard card.



Fig. S16 (a)-(c) SEM images and (d) EDS spectrum of Ni₃[Co(CN)₆]₂•12H₂O nanocubes.



Fig. S17 XRD pattern of (Co-Ni)P@CC derived from Ni₃[Co(CN)₆]₂ \cdot 12H₂O nanocubes together

with XRD standard cards of CoP (01-089-4862) and Ni_5P_4 (00-018-0883).



Fig. S18 (a)-(b) SEM images and (c) EDS spectrum of (Co-Ni)P@CC derived from Ni₃[Co(CN)₆]₂•12H₂O nanocubes.



Fig. S19 SEM images: (a)-(b) Ni₃[Co(CN)₆]₂•12H₂O hollow nanocubes and (c)-(d) E-(Co-Ni)P@CC hollow nanocubes.

When Ni₃[Co(CN)₆]₂•12H₂O nanocubes were employed as the starting material, the thermal phosphorization product was composed of Ni₅P₄ (ICDD No. 00-018-0883) and CoP (ICDD No. 01-089-4862) nanoparticles embedded in N-doped C (Fig. S16-S18), with the cube shape well maintained. Moreover, Ni₃[Co(CN)₆]₂•12H₂O nanocubes were also treated with ammonia etching to produce Ni₃[Co(CN)₆]₂•12H₂O carved hollow nanocubes, which serve as the precursor to create E-(Co-Ni)P@CC hollow nanocubes through thermal phosphorization (Fig. S19).



Fig. S20 Polarization curves of (a) RuO₂ toward OER and (b) Pt/C toward HER.



Fig. S21 Negative scan polarization curve of E-(Fe-Ni)P@CC/(Co-Ni)P@CC toward OER.



Fig. S22 Reduction peaks recorded at 300 mV/s for determination of numbers of surface active sites: (a) E-(Fe-Ni)P@CC/(Co-Ni)P@CC, (b) (Fe-Ni)P@CC/(Co-Ni)P@CC, (c) (Fe-Ni)P@CC, (d) E-(Co-Ni)P@CC, (e) (Co-Ni)P@CC, and (f) E- (Fe-Ni)P@CC.



Fig. S23 Photograph of overall water splitting set-up, powered by a 1.5 V battery, using E-(Fe-Ni)P@CC/(Co-Ni)P@CC as catalyst for both cathode and anode.



Fig. S24 SEM images of E-(Fe-Ni)P@CC/(Co-Ni)P@CC after (a) HER and (b) OER.



Fig. S25 XPS spectra of E-(Fe-Ni)P@CC/(Co-Ni)P@CC after HER: (a) Ni, (b) Co, (c) Fe, and (d)

P.



Fig. S26 XPS spectra of E-(Fe-Ni)P@CC/(Co-Ni)P@CC after OER: (a) Ni, (b) Co, (c) Fe, and (d)

P.



Fig. S27 Amounts of H_2 and O_2 experimentally measured and theoretically calculated versus time at current density of 50 mA/cm².



Fig. S28 Cyclic voltammograms recorded at increasing scan rates in 1 M KOH: (a) E-(Fe-Ni)P@CC/(Co-Ni)P@CC, (b) (Fe-Ni)P@CC/(Co-Ni)P@CC, (c) (Fe-Ni)P@CC, (d) E-(Co-Ni)P@CC, (e) (Co-Ni)P@CC, and (f) E-(Fe-Ni)P@CC. (g) Linear fitting of current density difference (recorded at 0.93 V vs. RHE) *vs.* scan rate in 1.0 KOH to determine C_{dl}. Colour codes: black for E-(Fe-Ni)P@CC/(Co-Ni)P@CC, red for (Fe-Ni)P@CC/(Co-Ni)P@CC, blue for (Fe-Ni)P@CC, green for E-(Co-Ni)P@CC, magenta for (Co-Ni)P@CC, and cyan for E- (Fe-Ni)P@CC.

Catalysts	η ₁₀ (mV)	Tafel slope (mV/dec)	C _{dl} (mF/cm²)
E-(Fe-Ni)P@CC/(Co-Ni)P@CC	204	44	4.29
(Fe-Ni)P@CC/(Co-Ni)P@CC	216	52	3.49
(Fe-Ni)P@CC	250	60	3.02
E-(Co-Ni)P@CC	305	68	2.35
(Co-Ni)P@CC	327	85	1.85
E-(Fe-Ni)P@CC	380	127	1.05

Table S1 Summary of OER performances of six electrocatalysts

Table S2 Summary of HER performances of six electrocatalysts

Catalysts	η ₁₀ (mV)	Tafel slope (mV/dec)
E-(Fe-Ni)P@CC/(Co-Ni)P@CC	129	88
(Fe-Ni)P@CC/(Co-Ni)P@CC	169	111
(Fe-Ni)P@CC	195	125
E-(Co-Ni)P@CC	201	146
(Co-Ni)P@CC	214	174
E-(Fe-Ni)P@CC	229	288

Catalysts	Loading Mass	η_{10}	Tafel slope	Reference
E-(Fe-Ni)P@CC/(Co-Ni)P@CC	(mg/cm ⁻) 0.5	$(m v)$ 204 $(\eta_{50} = 235)$ $(\eta_{100} = 249)$ $(\eta_{250} = 277)$	(mv/dec) 44	This work
Hierarchical Ni-Co-P HNBs	2	270	76	Energy Environ. Sci., 2018, 11, 872
NiFe-LDH@NiCu	0.4	218	56.9	Adv. Mater., 2019, 31, 1806769
Co ₂ P NCs	N/A	280	60.4	Adv. Mater., 2018, 30, 1705796
$Ni_{0.6}Co_{1.4}P$ nanocages	0.35	300	80	Adv. Funct. Mater., 2018, 28, 1706008
FeMnP nanoplatelet	2.4	230	35	Nano Energy, 2017, 39, 444
Fe-CoP	0.4	302	N/A	J. Mater. Chem. A, 2018, 6, 4783
Fe-Co-2.3Ni-B nanoparticle	0.3	274	38	Adv. Energy Mater., 2018, 8, 1701475
NiCoP/C	1.0	330	96	Angew. Chem. Int. Ed., 2017, 56, 3897
Ni-Fe LDH hollow nanoprisms	0.16	280	49.4	Angew. Chem. Int. Ed., 2018, 57, 172
Porous Ni-Fe-P@C	N/A	217	40	J. Mater. Chem. A, 2017, 5, 2496

Table S3 Comparison of OER performances in 1 M KOH: present work vs. literature.

Catalysts	Loading Mass (mg/cm ²)	η ₁₀ (mV)	Tafel slope (mV/dec)	Reference
E-(Fe-Ni)P@CC/(Co-Ni)P@CC	0.5	129 ($\eta_{50} = 220$) ($\eta_{100} = 245$) ($\eta_{250} = 284$)	88	This work
NiCoFe-LDHs	0.3	η ₄₀ =200	78	J. Mater. Chem. A, 2016, 4, 7245
Ni _{1.5} Fe _{0.5} P	0.2	264	55	Nano Energy, 2017, 34 472
Co/CoP-5	0.22	253	73.8	Adv. Energy Mater., 2017, 7, 1602355
CuCoP/nitrogen doped carbon	0.4	220	122	Adv. Energy Mater., 2017, 7, 1601555
NiFe LDH/NiCo ₂ O ₄ /NF	4.9	192	59	ACS Appl. Mater. Interf., 2017, 9, 1488
NDGL coated Fe-Ni alloy nanoparticles encapsulated in NDCHN	0.5	201	133.2	Nano Energy, 2018, 48, 489
FeP/NF	1	165	97	Chem. Sci., 2018, 9, 8590
CoP/rGO-400	0.28	150	38	Chem. Sci., 2016, 7, 1690
FeNiP/PG	0.51	173	50.3	J. Mater. Chem. A, 2019,7, 14526-14535
Fe-Ni@NCCNTs	0.5	202	113.7	Angew. Chem. Int. Ed., 2018, 57, 8921
CoNiP microspheres	N/A	145.8	52	J. Mater. Chem. A, 2019, 7, 8602
Cr-doped FeNi-P/NCN	0.48	190	68.51	Adv. Mater., 2019, 31, 1900178

Table S4 Comparison of HER performances in 1 M KOH: present work vs. literature.

Catalysts	Voltage at 10 mA cm ⁻² (V)	Reference
E-(Fe-Ni)P@CC/(Co-Ni)P@CCl E-(Fe-Ni)P@CC/(Co-Ni)P@CC	1.57	This work
$Ni_{1.5}Fe_{0.5}P Ni_{1.5}Fe_{0.5}P $	1.589	Nano Energy, 2017, 34 472
NiS/Ni ₂ P/CClNiS/Ni ₂ P/CC	1.67	ACS Appl. Mater. Interf., 2018, 10, 4689
$Ni_5P_4 Ni_5P_4 $	1.7	Angew. Chem. Int. Ed., 2015, 54, 12361
Ni-Co-P HNBsINi-Co-P HNBs	1.62	Energy Environ. Sci., 2018, 11, 872
NiS/Ni ₂ P/CCINiS/Ni ₂ P/CC	1.62	J. Mater. Chem. A, 2018, 6, 8233.
Co-P/N-doped carbon matrices Co-P/N-doped carbon matrices	1.7	Chem. Mater., 2015, 27, 7636
Ni-Co-P hollow nanobricks Ni-Co-P hollow nanobricks	1.77	Energy Environ. Sci., 2018, 11, 872.
NDGL coated Fe-Ni alloy nanoparticles encapsulated in NDCHNINDGL coated Fe-Ni alloy nanoparticles encapsulated in NDCHN	1.701	Nano Energy, 2018, 48, 489

Table S5 Comparison of electrochemical performances for overall water splitting in 1 M KOH:

 present work vs. literature.