Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

$Fe_xNi_{4-x}P_y$/N, P Codoped Carbon Nanotubes Composite as A Bifunctional Electrocatalyst for Oxygen and Hydrogen Electrode Reactions

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Experimental section

Materials

Melamine (AR, 99%), $NiCl_2 \cdot 6H_2O$ (AR, 99%) and IrO_2 (99.9%, metals basis) were purchased from Macklin company. $NaH_2PO_4 \cdot H_2O$ (AR, 99%) and $FeCl_3 \cdot 6H_2O$ (AR, 99%) were obtained from shanghai Aladdin Biochemical Technology Co. Ltd. All the reagents were not further purification.

Synthesis of $Fe_xNi_{4-x}P_y$/N, P-CNTs electrocatalysts

In a typical procedure, 1.00 g of melamine was well dispersed in 40 mL of deionized water by vigorously stirring for 10 min. Then, 0.10 g of $FeCl_3 \cdot 6H_2O$ and 0.10 g of $NiCl_2 \cdot 6H_2O$ were added to the above solution. After continuously stirring for 24 h, the resultant precipitates were centrifuged and fully washed with deionized water and ethyl alcohol. Afterwards, the collected products were vacuum dried at 80 °C for 4 h. The yellow product was fully ground and put into a tube furnace and heated to 850 °C with a heating rate of 5 °C /min in an Ar (99.999%) gas flowing. After keeping at this temperature for 1 h, the products were collected. Next, 2.0 g of $NaH_2PO_4 \cdot H_2O$ was placed at the upstream side of tube furnace, and the 50 mg of the above prepared precursor was placed at the downstream side. Then, the samples were maintained at 450 °C for 3 h under an Ar atmosphere. After cooling to the room temperature naturally, the catalyst was collected and used directly for electrochemical measurements.

Characterizations

The morphologies and phases of the as-synthesized catalysts were obtained by scanning electron microscopy (SEM, Hitachi High-Technology Co., Ltd, Japan),

transition electron microscopy (TEM, JEOL JEM-2100, Japan), and X-ray diffraction (XRD, D/Max2000, Rigaku, Japan). The chemical valence and composition of the as-synthesized material was investigated by X-ray photoelectron spectroscopy (XPS, Escalab 250 xi). X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were conducted with a BL 10C beamline at Pohang Light Source (Korea) operated at 3.0 GeV with a 200 mA ring current.

Electrochemical Measurements

The electrochemical tests (OER, HER) were conducted at a CHI 760E electrochemical workstation in a standard three-electrode system with glassy carbon electrode coated with electrocatalyst as the working electrode, reversible hydrogen electrode as the reference electrode, and carbon rod as the counter electrode. 1 M KOH was used as the electrolyte. The catalyst ink was prepared as the following step: 3 mg of the catalysts were dispersed into 0.3 mL of ethanol, 0.15 mL ultra deionized water, and 60 μL of Nafion solution by sonication for 30 min. Then, 5 μL of the catalyst ink was transferred onto the glassy carbon and dried at room temperature to form a catalyst layer. The catalyst loading is 0.4 mg cm^{-2}.

All the LSV curves were measured at a scan rate of 5 mV s^{-1} within a potential range of 1.3 – 1.7 V (vs RHE) for OER and 0 - -0.5 V (vs RHE) for HER. All the data were calibrated relatively to reversible hydrogen electrode (RHE) with 95 % iR compensation. The electrochemical impedance was measured with amplitude of 5 mV in a frequency range from 100 kHz to 0.1 Hz at the open-circuit voltage. The C_{dl} was measured in a non-Faradaic potential window from 1.05 V- 1.15 V (vs RHE).

Overall water splitting. The overall water splitting performance of the prepared $Fe_xNi_{4-x}P_y$/N, P-CNTs as both anode and cathode was investigated in a two-electrode cell. The 1.0 M KOH solution was used as electrolyte. The testing voltage ranges from 0.9 V to 2.2 V. The polarization curves were measured at a scan rate of 5 mV s^{-1}.

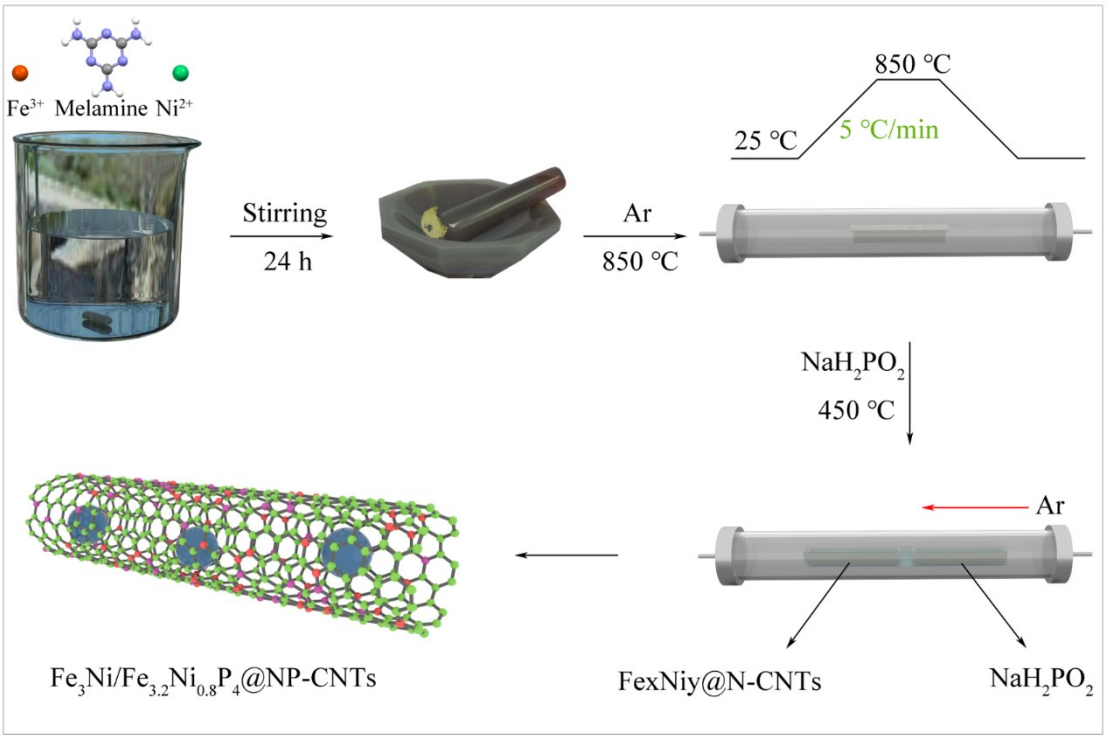

Figure S1. A scheme of the preparation of $Fe_xNi_{4-x}P_y$/N, P-CNTs electrocatalysts.

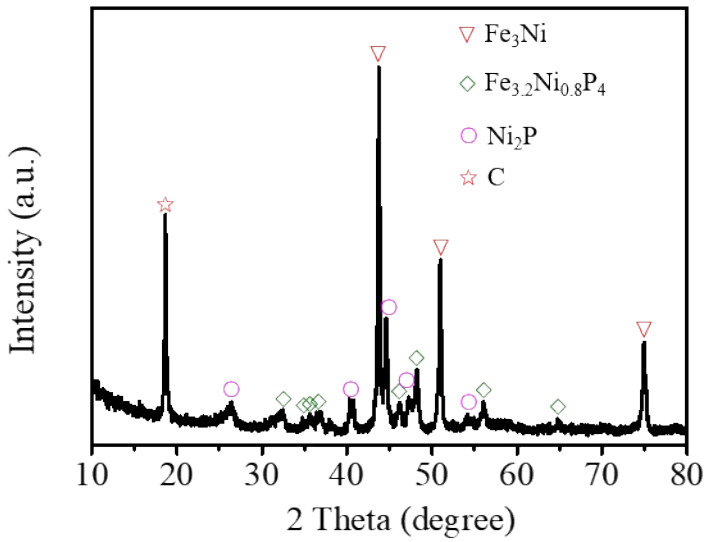

Figure S2. The XRD pattern of the prepared $Fe_xNi_{4-x}P_y$/N, P-CNTs catalyst.

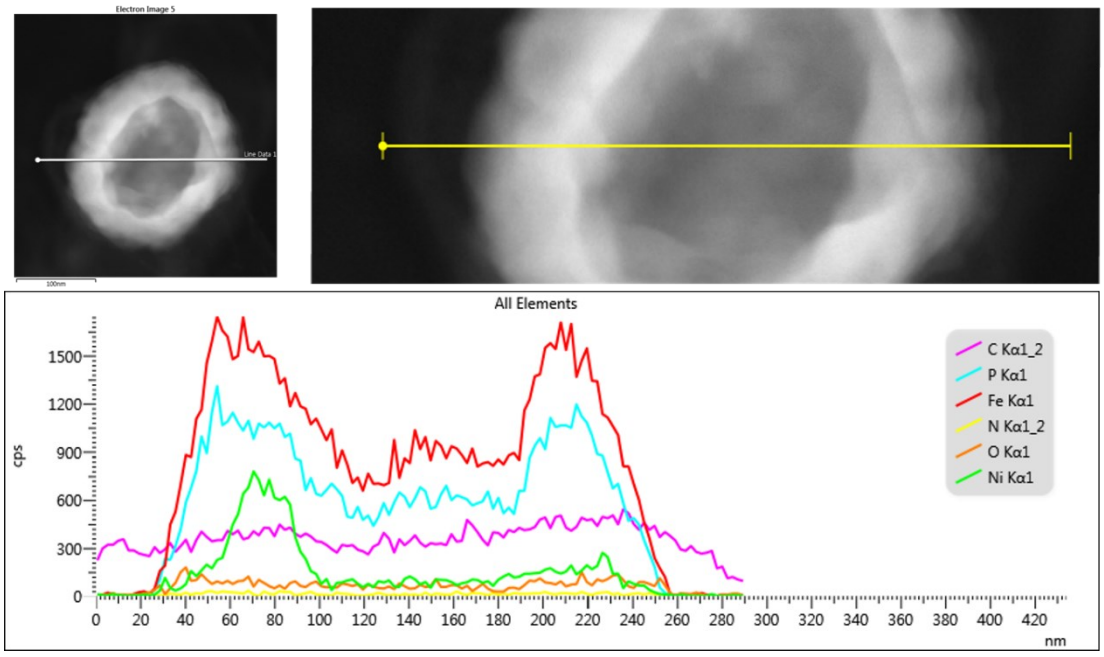

Figure S3. The linear distributions of C, P, Fe, N, O, Ni elements.

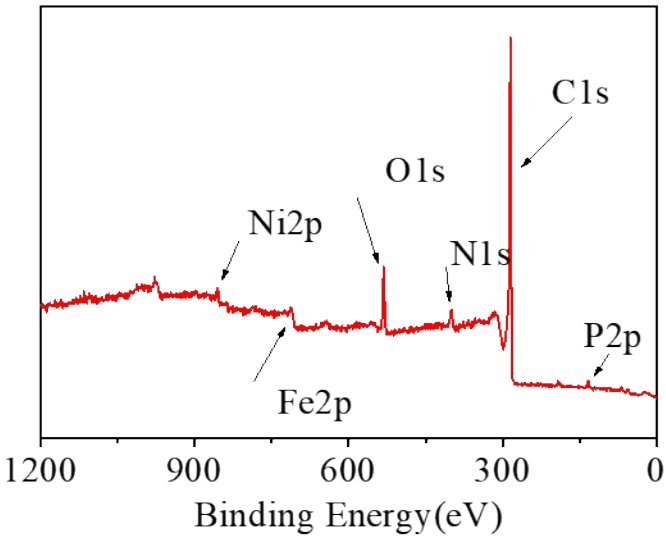

Figure S4. The XPS survey spectrum of $Fe_xNi_{4-x}P_y$/N, P-CNTs catalyst.

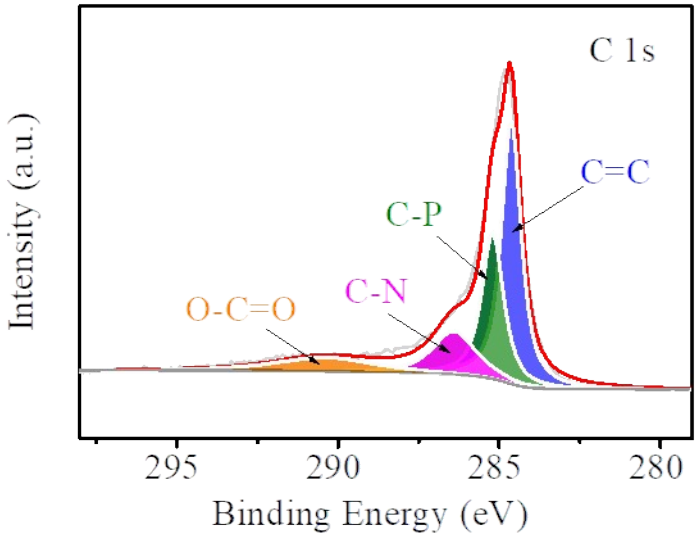

Figure S5. C 1s XPS spectrum of $Fe_xNi_{4-x}P_y$/N, P-CNTs catalyst.

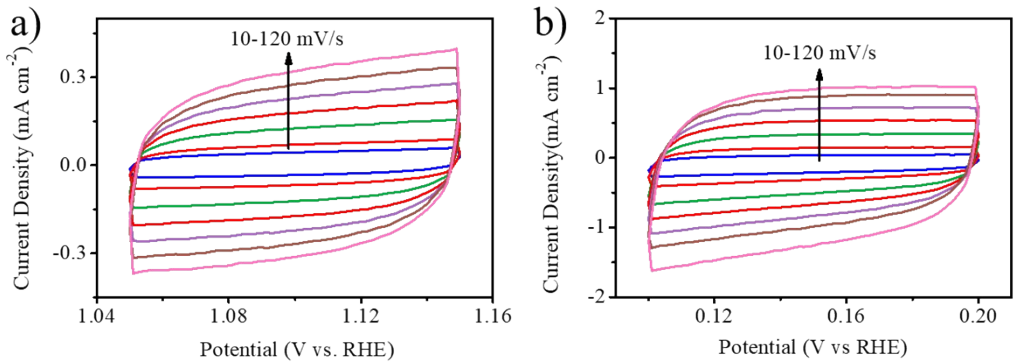

Figure S6. CV curves recorded at different scan rates for Fe_xNi_y/N-CNTs: a) OER, b) HER.

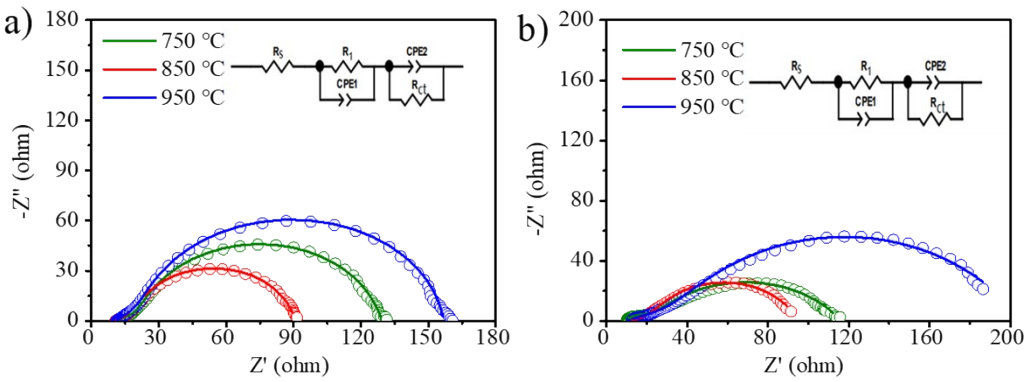

Figure S7. Nyquist plots measured in a range of 100 kHz- 0.1 Hz and the equivalent circuit. The equivalent circuit contains a resistor (R_s), in series with two parallel units of a constant phase element (CPE_1, CPE_{ct}) and a resistor (R_1, R_{ct}), where R_s represents the solution resistance, R_1-CPE_1 is probably related to the interfacial resistance resulting from the electron transport between the catalysts and GCE, and R_{ct}-CPE_{ct} reflects the charge transfer resistance at the interface between catalysts and the electrolyte.

Table S1. Electrochemical impedance parameters obtained simulating the Nyquist plots to the equivalent circuit model in Fig. S7a.

Catalyst	R_s (ohm)	CPE_1 –T (F)	CPE_1 - P (F)	R_1 (ohm)	CPE_2 –T (F)	CPE_2 - P (F)	R_{ct} (ohm)
750 ℃	10.69	0.00504	0.35002	19.06	0.00033572	0.91419	100.5
850 ℃	10.49	0.0057229	0.41297	16.12	0.00060253	0.93564	64.83
950 ℃	11.24	0.0013556	0.57283	13.72	0.00034224	0.93755	131.2

Table S2. Electrochemical impedance parameters obtained simulating the Nyquist plots to the equivalent circuit model in Fig. S7b.

Catalyst	R_s (ohm)	CPE_1 –T (F)	CPE_1 - P (F)	R_1 (ohm)	CPE_2 –T (F)	CPE_2 - P (F)	R_{ct} (ohm)
750 ℃	8.942	0.00026101	0.53515	14.28	0.0010774	0.63561	92.9
850 ℃	11.58	0.013298	0.28568	23.35	0.0035371	0.80668	63.03
950 ℃	9.788	0.0066046	0.27191	62.9	0.0018088	0.77408	141.6

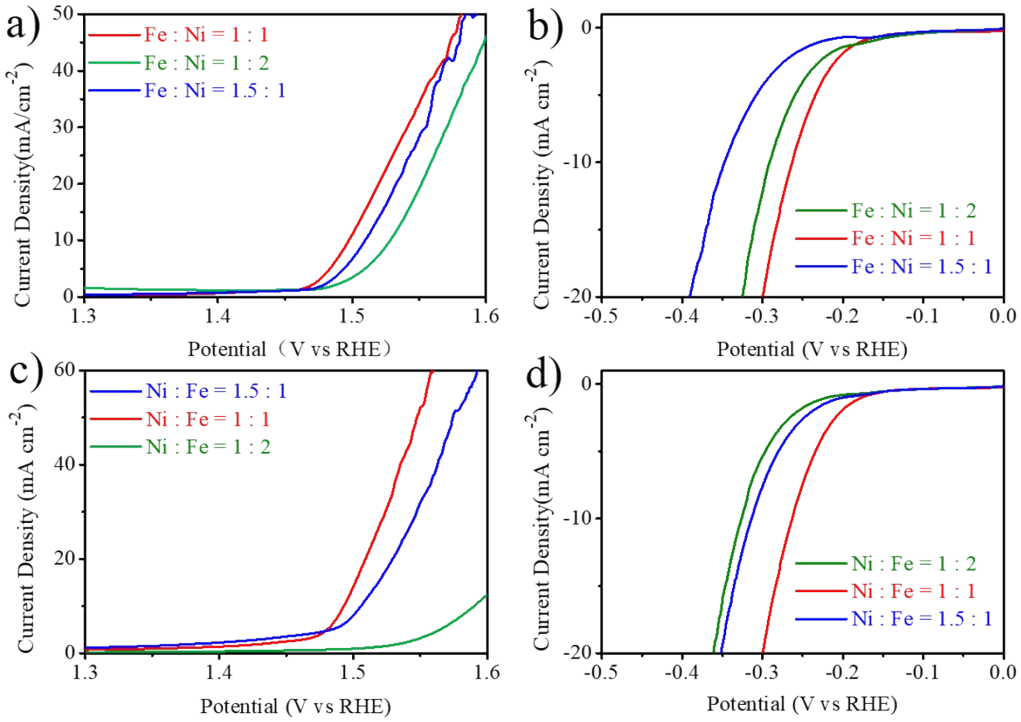

Figure S8. LSV curves of the catalysts prepared with different metal salt usage in 1.0 M KOH with iR compensation: a, c) OER, b, d) HER.

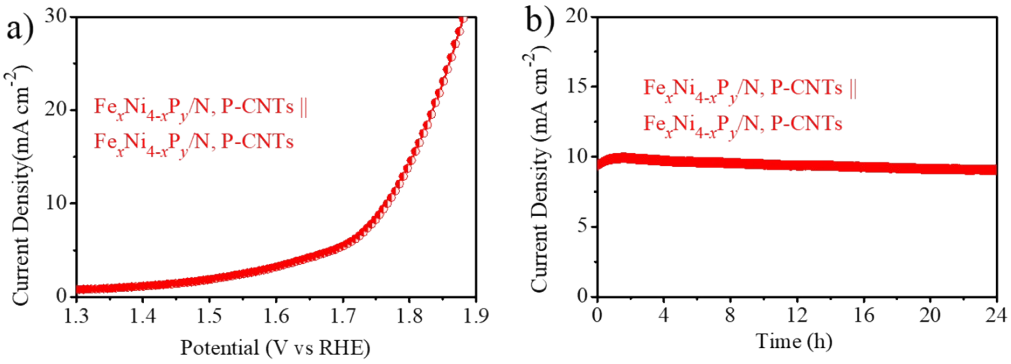

Figure S9. a) LSV curve of $Fe_xNi_{4-x}P_y$/N, P-CNTs || $Fe_xNi_{4-x}P_y$/N, P-CNTs for overall water splitting in 1.0 M KOH electrolyte. b) The durability test at a constant voltage of 1.76 V for 24 h.