## **Electronic Supplementary Information**

## **Experimental Section**

**Materials:** KOH, NH<sub>4</sub>F, and urea were purchased from Beijing Chemical Corp.  $H_2PtCl_6 \cdot 6H_2O$  and NiCl<sub>2</sub> $\cdot 6H_2O$  were purchased from Aladdin Ltd (China). Pt/C (20 wt% Pt) was provided by Alfa Aesar (China) Chemicals Co. Ltd. Nafion (5 wt%) was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. All the chemicals in the experiments were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

**Preparation of Ni(OH)**<sub>2</sub> **NA/CC:** In a typical synthesis, 2.25 mmol NiCl<sub>2</sub>·6H<sub>2</sub>O, 10 mmol urea, and 4 mmol NH<sub>4</sub>F were dissolved in 40 mL ultrapure water under vigorous stirring for 20 min. Then mixture solution and a piece of CC (3 cm  $\times$  2 cm) were transferred into a Teflon-lined stainless autoclave (50 mL), and maintained at 120 °C for 6 h in an electric oven. After the autoclave cooled down naturally, the resulting Ni(OH)<sub>2</sub> NA/CC was taken out and washed with ultrapure water.

**Preparation of PtNi-Ni NA/CC:** Firstly, the Ni(OH)<sub>2</sub> NA/CC were immersed in 25 mL H<sub>2</sub>PtCl<sub>6</sub> aqueous solution (0.08 mg mL<sup>-1</sup>). And then they were transferred into a 40 mL Teflon-lined stainless-steel autoclave and hydrothermally treated at 120 °C for 4 h. Finally, the resulting PtO<sub>2</sub>-Ni(OH)<sub>2</sub> NA/CC was placed in the furnace and heated to 400 °C with a heating speed of 5 °C min<sup>-1</sup> under a flowing H<sub>2</sub>/Ar atmosphere. After reacting 2 h at 400 °C, the system was allowed to cool down to room temperature naturally still under a flowing H<sub>2</sub>/Ar atmosphere. Finally, the black PtNi-Ni NA/CC was collected for further characterization.

**Preparation of Ni NA/CC:** The  $Ni(OH)_2$  NA/CC was placed in the furnace and treated under the same hydrogen reduction reaction conditions as above.

**Preparation of PtNi/CC and PtNi-Ni/CC:** PtNi alloy nanoparticles were synthesized according to a previously reported method.<sup>1</sup> Typically, 351.0 mg of  $K_2PtCl_6\cdot 6H_2O$ , 225.8 mg of NiCl\_2 $\cdot 6H_2O$ , and 777.8 mg of Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> were added to 200 mL of ethylene glycol to form a mixture in a three-necked flask and then the pH of the mixture was adjusted to 11 with 1 M KOH. Subsequently, the mixture was

heated to 180 °C for 6 h under a N<sub>2</sub> atmosphere. After cooling down to room temperature, the mixture was filtered, washed and dried to obtain PtNi alloy nanoparticles. To prepare PtNi ink, 40 mg PtNi alloy nanoparticles and 10  $\mu$ L 5 wt% Nafion solution were dispersed in 1 mL water/ethanol solvent (v:v = 1:1) with sonication for 30 min. Then 22.5  $\mu$ L catalyst ink was loaded on bare CC and Ni NA/CC (1 cm<sup>2</sup>) with a catalyst loading of 0.9 mg cm<sup>-2</sup>.

**Preparation of Pt/C on CC:** To obtain commercial Pt/C loaded electrodes, Pt/C ink was prepared as above. Then 22.5  $\mu$ L catalyst ink was coated onto bare CC (1 cm<sup>2</sup>) with a catalyst loading of 0.9 mg cm<sup>-2</sup>.

**Characterizations:** XRD data was performed using a LabX XRD-6100 X-ray diffractometer Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM measurements were collected on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were carried out on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. ICP-MS analysis was performed on ThermoScientific iCAP6300.

**Electrochemical measurements:** Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using PtNi-Ni NA/CC as the working electrode, a graphite rod as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Given that as-measured reaction currents do not directly reflect the intrinsic behavior of catalysts due to the effect of ohmic resistance, an *iR* correction was applied to all LSV curves for further analysis, and all potentials were reported on a reversible hydrogen electrode (RHE) scale unless specifically stated. The potentials reported in this work were calibrated to RHE, using the following equation: E (RHE) = E (SCE) + (0.242 + 0.059 pH) V = E (SCE) + 1.009 V. Polarization curves were obtained using linear sweep voltammetry with a scan rate of 5 mV s<sup>-1</sup>. All experiments were carried out at room temperature (~25 °C).

**FE determination:** The FE was calculated by comparing the amount of measured H<sub>2</sub> generated by potentiostatic cathode electrolysis with calculated H<sub>2</sub> (assuming 100% FE). GC analysis was carried out on GC-2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. Pressure data during electrolysis were recorded using a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of 1 point per second.

**TOF calculation:** The electrochemical active surface area (ECSA) is calculated using the following equation:

$$ECSA = C_{dl} / C_s$$
$$TOF = (j \times 3.12 \times 10^{15}) / (surface sites \times ECSA)$$

Where  $C_{dl}$  is the electrochemical double-layer capacitance,  $C_s$  is specific capacitance, j is current density during the LSV measurement in 0.1 M KOH.



Fig. S1. SEM images of (a,b) PtO<sub>2</sub>-Ni(OH)<sub>2</sub> NA/CC and (c,d) Ni(OH)<sub>2</sub> NA/CC.



Fig. S2. EDX spectrum for PtNi-Ni NA/CC.



Fig. S3. SEM image of bare CC.



Fig. S4. Cross-section SEM image of PtNi-Ni NA/CC.



Fig. S5. SEM images of Ni NA/CC.

Catalyst	j (mA cm <sup>-2</sup> )	η (mV)	Pt content (wt%)	Electrolyte	Refs.
PtNi-Ni NA/CC	5	21	7.7	0.1 M KOH	This
	10	38			work
Pt <sub>3</sub> Ni <sub>3</sub> NWs/C	10	45	76.9	0.1 M KOH	2
Pt <sub>3</sub> Ni frames/Ni(OH) <sub>2</sub> /C	5	63	20	0.1 M KOH	3
hcp-Pt-Ni	10	66	39.6	0.1 M KOH	4
Ni <sub>3</sub> N/Pt	10	50	15	1.0 M KOH	5
Pt <sub>3</sub> Ni <sub>2</sub> NWs-S/C	10	45	81.6	0.1 M KOH	6
Pt-Ni/C	10	68	25	0.1 M KOH	7
Pt <sub>13</sub> Cu <sub>73</sub> Ni <sub>14</sub> /CNF@CF	10	67	1.8	1.0 M KOH	8
PtNi alloy nanohexapod	5	22	18.1	0.1 M KOH	9
$Ru_1@Pt_{1.0}(2ML)$	10	129	59.7	1.0 M KOH	10
Pt NWs/SL-Ni(OH) <sub>2</sub>	10	48	38	0.1 M KOH	11
Ni(OH) <sub>2</sub> /Pt-islands/Pt(111) surface	10	138	Pt electrode	0.1 M KOH	12
Pt(111)-Co(OH) <sub>2</sub>	3	196	Pt electrode	0.1 M KOH/LiOH	13

**Table S1.** Comparison of HER performance for PtNi-Ni NA/CC with other Pt-based
 electrocatalysts in alkaline electrolytes.



Fig. S6. SEM images of (a,b) PtNi/CC and (c,d) PtNi-Ni/CC.



**Fig. S7.** Cyclic voltammograms for (a) PtNi-Ni NA/CC, (b) PtNi-Ni/CC, and (c) PtNi/CC. (d) The capacitive current densities at 0.815 V as a function of scan rate for PtNi-Ni NA/CC, PtNi-Ni/CC, and PtNi/CC.

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