Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Electronic Supplementary Information

Chemical induced fragmentation of MOFs for highly efficient Ni-based hydrogen evolution catalysts

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Experimental details

Preparation of the $Ni_2(bdc)_2(ted)$ and $Ni_xCo_{2-x}(bdc)_2(ted)$. 1,4-benzenedicarboxylic acid (H_2BDC, 0.70g, 4.2 mmol, J&K Chemicals co. ltd.), Triethylene-diamine (TED, 0.22g, 2.0mmol, J&K Chemicals co. ltd.), and $Ni(NO_3)_2 \cdot 6H_2O$ (1.2 g, 4.1 mmol, Xilong Chemicals co. ltd.) are dissolved in 50 mL DMF (Xilong Chemicals co. ltd.). The solution is sealed in a 100 mL Teflon-lined autoclave and kept at 130 °C for 24h. The obtained green crystalline powders are washed with DMF for two times and ethanol for another two times, and dried at 60 °C in vacuum overnight. The $Ni_xCo_{2-x}(bdc)_2(ted)$ is synthesized in the same way using the mixture of $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ (Xilong Chemicals co. ltd.).The total weight of the nitrate was also 1.2 g.

Preparation of the HER catalysts. The HER catalysts were prepared by temperature programmed pyrolysis of the $Ni_2(bdc)_2(ted)$ or $Ni_xCo_{2-x}(bdc)_2(ted)$ n different atmosphere. Typically, 0.2 g $Ni_2(bdc)_2(ted)$ or $Ni_xCo_{2-x}(bdc)_2(ted)$ was loaded into a quartz tube furnace. The system is flushed with Ar for 30 min to remove oxygen and moisture. The sample is heated to certain temperature at 10 °C min^{-1} in the desired atmosphere, kept at the peak temperature for 1 h, and allowed to cool down to room temperature in pure Ar flow.

Materials characterization. The content of C and N was decided by the combustion method (Vario EL elemental analyzer). The structure and morphology of the products are characterized by X-ray diffraction (XRD, PANalytical X'Pert3 diffractometer, Cu Kα), and high-resolution transmission electron microscopy (HRTEM, JEM-2100, 200 kV). Thermogravimetric analysis (TGA) is carried out with N_2 atmosphere on a Q600 SDT thermoanalyzer (Thermal Analysis Corporation, USA). Nitrogen adsorption-desorption isotherms were measured on a NOVA 2200 gas sorption analyzer (Quantachrome) at 77 K. Before testing, samples were degassed at 150 °C for 12 h. The surface area were determined by the Brunauer–Emmett–Teller (BET) method. The X-ray photoelectron spectroscopy (XPS) analysis was performed on an AXIS-Ultra spectrometer (Kratos Analytical) using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low energy electron flooding for charge compensation. ^{13}C and ^{1}H NMR spectra are collected for liquid samples on a Bruker AVANCE III 400 MHz (for ^{1}H nuclei) spectrometer, All the NMR spectra were collected in dimethyl sulfoxide-d_6 as solvent and tetramethylsilane(TMS) as external standard. For *in-situ* Temperature programmed desorption-mass spectrometry (TPD-MS) measurement, when Ni-MOFs was heated in tube furnace with rising temperature, the gas flow through the furnace was directly induced to a Ominstar Pfeiffer Prisma Plus Mass Spectrometer-Residual Gas Analyser (MS-RGA). Two needle valves, a vent sampling valve and a mass spectrometer input valve, are adjusted to introduce an appropriate amount of gas into the mass spectrometer.

Electrode Preparation. To prepare the working electrode, 2 mg of catalyst powders were ultrasonically dispersed in a mixed solution of 100 µL Nafion (0.5 wt% in ethanol and water) for about 0.5 h. Then, 7 µL suspension was dropped onto a glassy carbon electrode (GCE) of 3.0 mm in diameter. The catalyst loading is 2 mg cm^{-2}. The electrode is dried for 2 h at room temperature.

Electrochemical Measurements. To All electrochemical measurement was performed in a standard three-electrode system controlled by a CHI 760D electrochemistry workstation. The working electrode is the catalyst loaded GCE. A clean platinum foil is used as counter electrode, and a saturated calomel electrode (SCE) is used as reference electrode. The electrolyte was N_2 saturated 1 M KOH solution. The linear scan voltammetry (LSV) was tested at a rate of 2 mV s^{-1} in a range from 0.02 V to -0.4 V (vs. RHE). CV scanning was carried out from -0.4 V to 0.1 V (vs. RHE) at a rate of 100 mV s^{-1} for 1000 and 2000 cycles in order to test the durability of the catalyst.

Galvanostatic electrolysis was measured under a constant current density of 20 mA cm^{-2} in an air-tight, three-electrode, single compartment electrolysis cell. A Ni foam substrate loaded with the catalyst(2 mg cm^{-2}) is used as working electrode. A clean platinum foil is used as counter electrode. A SCE electrode as reference electrode. The time dependent potential of the working electrode is recorded. During the chronopotentiometry test, the evolved hydrogen was introduced into the gas chromatography(GC), then quantified by the integrated areas of the peaks corresponding to hydrogen.

Preparation of the OER catalyst. The precursor of NiFe-based OER catalyst is FeNi-substituted ZIF-8, which is synthesized by direct reaction of 2-methylimidazole (Hmim, 40 mmol) and mixed metal acetates (3 mmol of ferrous acetate,1 mmol of nickel acetate and 6 mmol of zinc acetate) in oxygen-free methanol at room temperature. After the centrifugation, washing and drying process, the as-prepared precursor was heated to 1000 °C with and kept for 1 hour under a argon flow to obtain NiFe-based OER catalyst.

Solar-driven water electrolysis. Solar water electrolysis was performed on a home designed eletrolyzer with 1 M KOH solution added, while the power source is a commercial polycrystalline silicon solar cell (5.5× 5.5 cm^2). Both $Ni_{0.9}Co_{0.1}$-NH_3 HER catalyst and NiFe-based OER catalyst were loaded on 1.2× 2.0 cm^2 carbon cloth with a loading of 2 mg cm^{-2}. And the two electrodes were separated by a polypropylene membrane. The irradiation on solar cell from the Xe lamp was 100 mW cm^{-2} from measurement of a solar radiometer (Photoelectric Instrument of Beijing Normal University)

Table S1. Carbon, nitrogen and nickel composition of MOF-derived catalysts

	Ni-Ar	**Ni-NH_3**	**Ni-Ar-NH_3**	**Ni-H_2**
C (wt%)	33.1	2.3	31.3	29.6
N (wt%)	2.8	1.1	3.8	1.5
Ni (wt%)	50.2	88.1	51.4	55.6

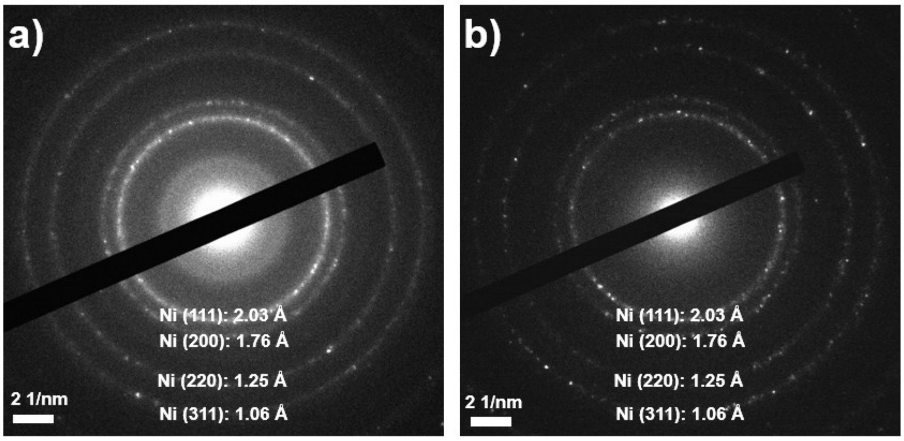

Figure S1. SAED image of a) Ni-Ar and b) Ni-NH_3 corresponding to Figure 2b and 2d repectively.

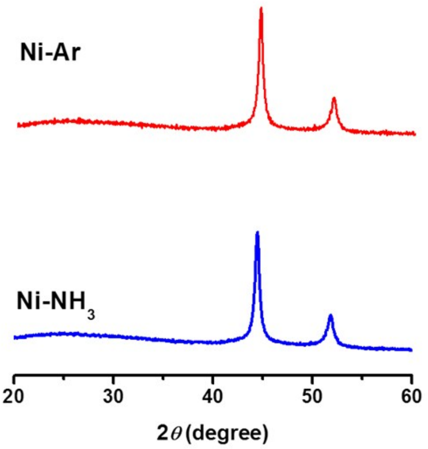

Figure S2. XRD patterns of Ni-Ar and Ni-NH$_3$

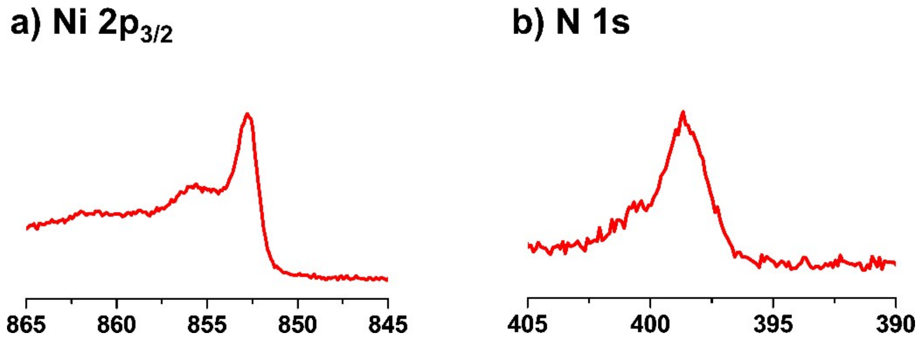

Figure S3. XPS spectra of Ni-NH$_3$

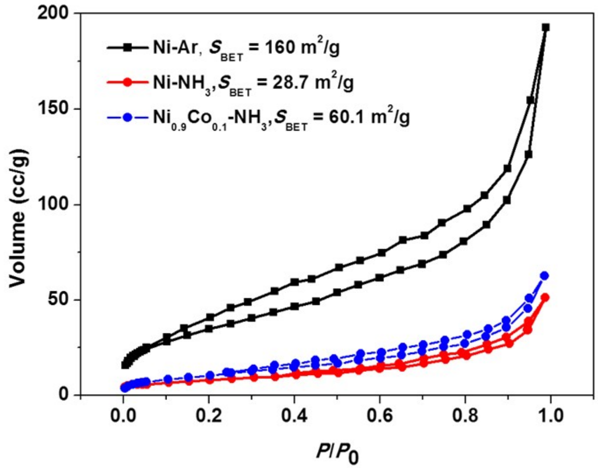

Figure S4 N_2 adsorption and desorption curve of Ni-Ar, Ni-NH$_3$ and Ni$_{0.9}$Co$_{0.1}$-NH$_3$ with surface area calculated from BET method.

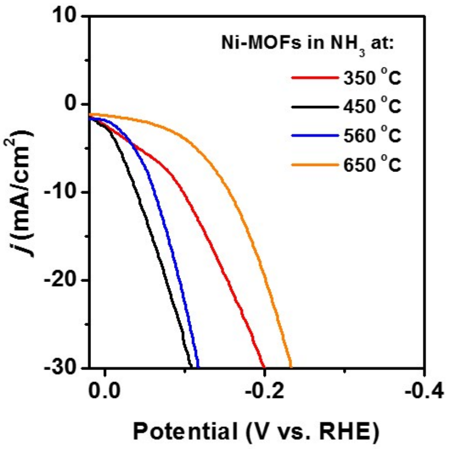

Figure S5. Linear polarization curves of catalyst derived from Ni-MOFs with different temperature under 20%NH_3-80%Ar atmosphere

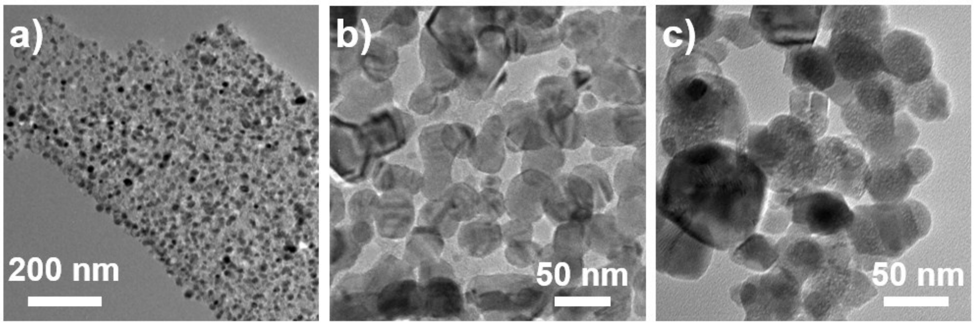

Figure S6 TEM images of catalyst derived from Ni-MOFs heated at a) 350 °C, b) 560 °C and c) 650 °C under 20%NH_3-80%Ar atmosphere

Table S2. Carbon, nitrogen and nickel composition of MOF-derived catalysts treated with different temperature under 20%NH_3-80%Ar atmosphere

temp	**350 °C**	**450 °C**	**560 °C**	**650 °C**
C (wt%)	34.5	2.3	1.2	0.4
N (wt%)	4.9	1.1	0.7	0.3
Ni (wt%)	32.0	88.1	94.9	96.1

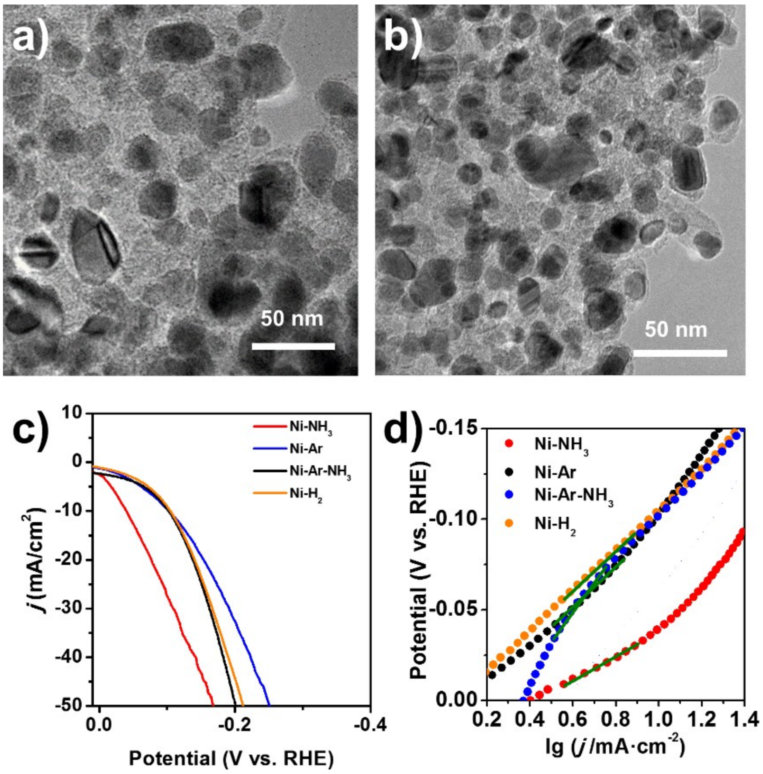

Figure S7. TEM image of a)Ni-Ar-NH$_3$ and b) Ni-H$_2$; c) linear polarization curve, d) Tafel plots of Ni-Ar, Ni-NH$_3$, Ni-H$_2$, and Ni-Ar-NH$_3$ catalysts in 1 M KOH.

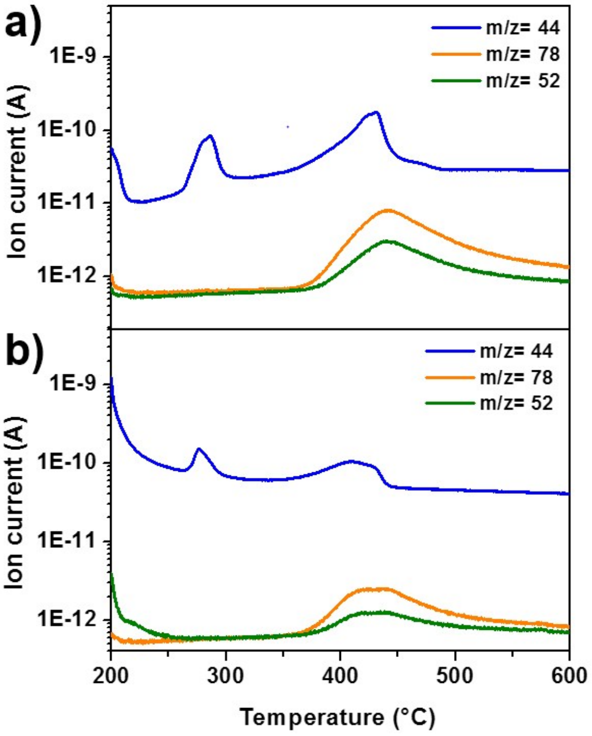

Figure S8 *in-situ* TPD-MS with m/z= 44,78,and 52 of a) Ni-Ar and b) Ni-NH$_3$

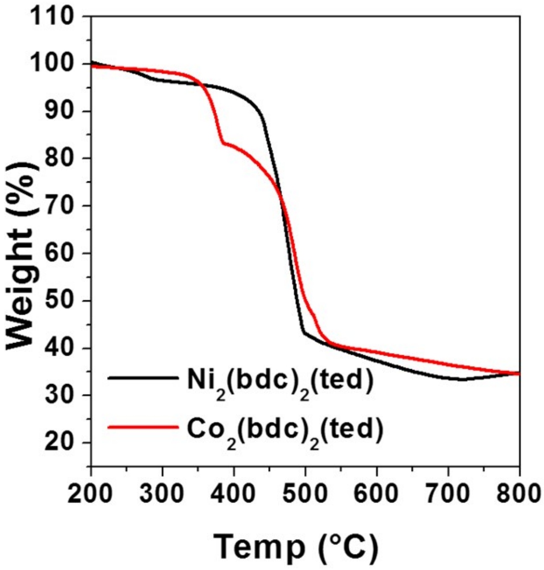

Figure S9 TGA curve of $Ni_2(bdc)_2(ted)$ and $Co_2(bdc)_2(ted)$ in N_2 atmosphere

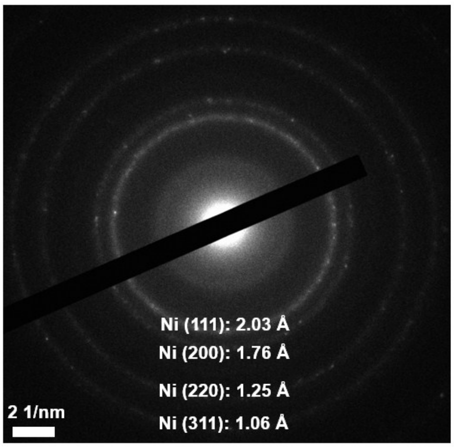

Figure S10. SAED image of $Ni_{0.9}Co_{0.1}$-NH_3 corresponding to Figure 4a.

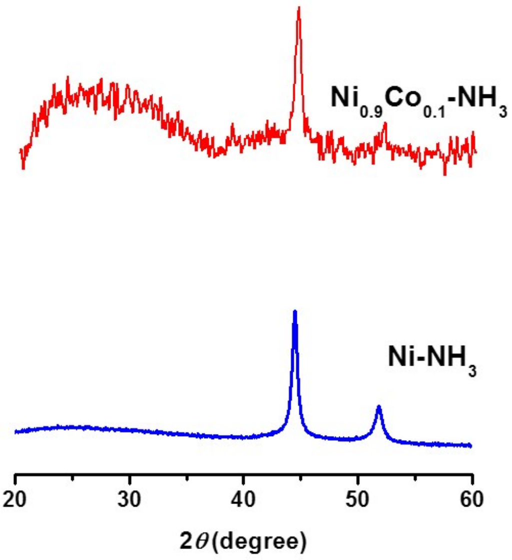

Figure S11. XRD patterns of Ni-NH_3 and $Ni_{0.9}Co_{0.1}$-NH_3 at 450 °C

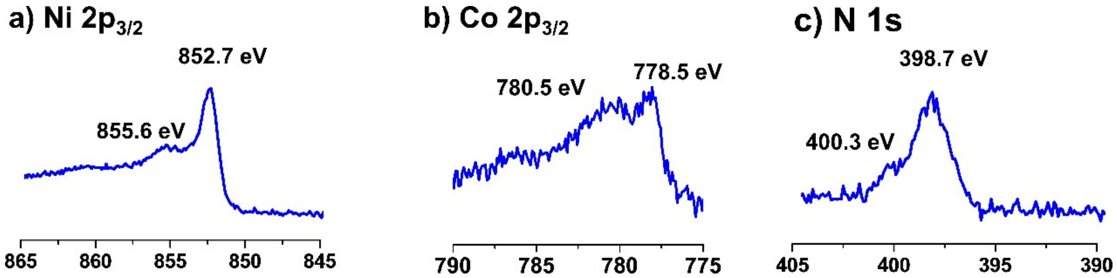

Figure S12 XPS spectra of $Ni_{0.9}Co_{0.1}$-NH_3

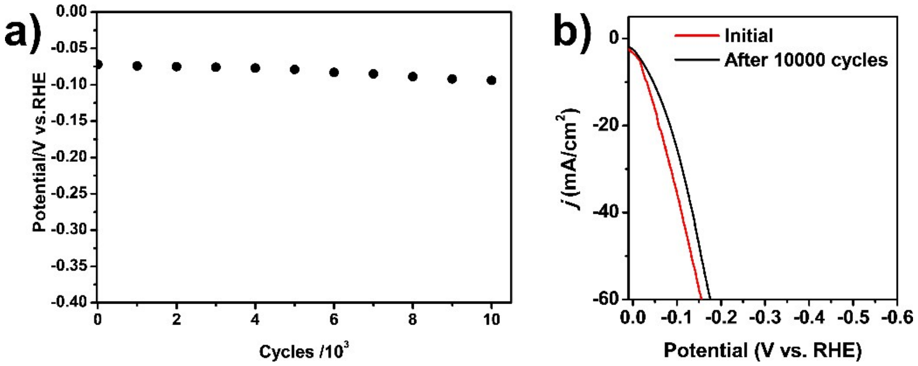

Figure S13 (a) the overpotential at 20 mA cm^{-2} (η_{20}) and (b) LSV curves after repeated CV cycles between -0.2 to 0.1 V of $Ni_{0.9}Co_{0.1}$-NH_3 catalyst

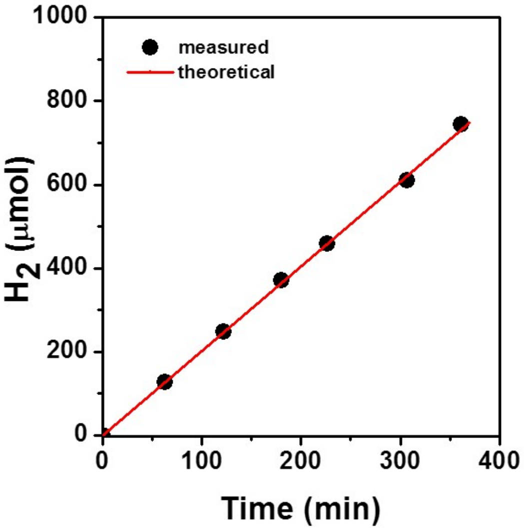

Figure S14 amount of H_2 generated by electrolysis of $Ni_{0.9}Co_{0.1}$-NH3 catalyst at 20 mA cm^{-2} in chronogalvanostatic electrolysis shown in Figure . The theoretical H_2 amount is shown as the straight line.

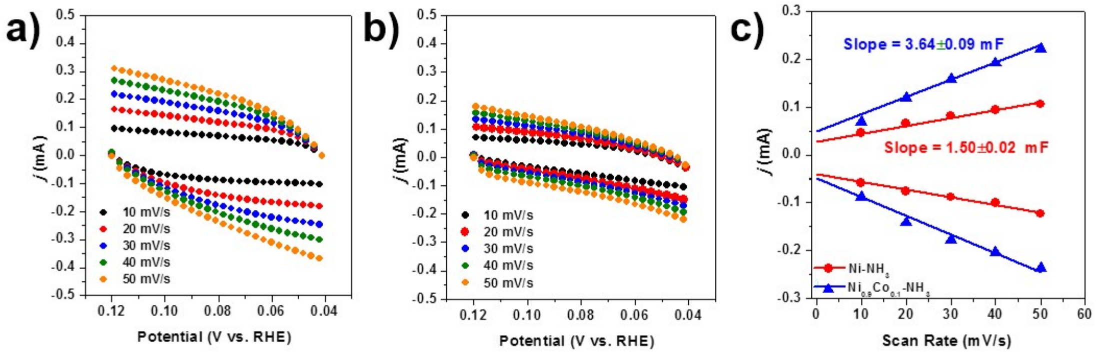

Figure S15 Cyclic voltammetry tests in region without hydrogen evolution (0.04 to 0.12 V vs RHE) with different scan rates to determine the electrochemical double layer capacitance (C_{dl}) of a) Ni-NH_3 and b) $Ni_{0.9}Co_{0.1}$-NH_3. c) the current vs scan rate (i_C-v) plots.

Table S3 Summary of the HER catalytic activity of representative metal-carbon nanocomposites in alkaline solutions

Catalyst	**Electrolyte**	**Loading (mg/cm^2)**	***η* (mV)**	***j* (mA·cm^{-2})**	**Ref.**
MOF-derived Ni-Co	1M KOH	2	36 58	10 20	This work
MOF-derived Ni	1M KOH	2	42 77	10 20	This work
Ni/NiO@ MWCNTs	1M KOH	0.28 8	80 95	10 100	[1]
MoC_x nano octahedron	1M KOH	0.8	151	10	[2]
Mo_xC-Ni@NCV	1 M KOH	1.1	126	10	[3]
Co@BCN	1 M KOH	not given	183	10	[4]
NiMoN@carbon cloth	1 M KOH	2.5	109	10	[5]
NanoMoC@GS	1 M KOH	0.76	77	10	[6]

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