

MOF-derived surface modified Ni nanoparticles as an efficient catalyst for the hydrogen evolution reaction

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Experimental section

Preparation of Ni₂(bdc)₂(ted)

1,4-benzenedicarboxylic acid (H₂bdc, 0.70g, 4.2 mmol, J&K Chemicals co. Ltd.), Triethylenediamine (ted, 0.22g, 2.0mmol, J&K Chemicals co. Ltd.), and Ni(NO₃)₂·6H₂O (1.2 g, 4.1 mmol, Xilong Chemicals co. Ltd.) were dissolved in 50 mL DMF (Xilong Chemicals co. Ltd.). The solution was sealed in a 100 mL Teflon-lined autoclave and kept at 130 °C for 24h. The obtained green crystalline powders were washed with DMF for two times and ethanol for another two times, and dried at 60 °C in vacuum overnight.

Preparation of the HER catalysts

The HER catalysts were prepared by temperature programmed pyrolysis of the Ni₂(bdc)₂(ted) in different atmosphere. Typically, 0.2 g Ni₂(bdc)₂(ted) was loaded into a quartz tube furnace. The system was flushed with Ar for 30 min to remove oxygen and moisture. The sample was heated to 560 °C 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. The pyrolysis atmosphere used in our study is given in Table 1 with the corresponding designation of the samples.

Materials characterizations

The content of C and N was decided by the combustion method (Vario EL elemental analyzer). The content of Ni was obtained using inductively coupled plasma-atomic emission spectrometer (ICP-AES) performed on a CCD-ICP-AES spectrometer (PROFILE SPEC). The samples were first calcinated in air at 900 °C for 12 h. Then the obtained residue was dissolved in 2 mol L⁻¹ HNO₃ to

give the solution for ICP-AES analysis. The structure and morphology of the products were characterized by X-ray diffraction (XRD, Rigaku D/max 2000 diffractometer, Cu K α), and high-resolution transmission electron microscopy (HRTEM, JEM-2100, 200 kV). Thermogravimetric analysis (TGA) was carried out 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 was 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 K α radiation (225 W, 15 mA, 15 kV) and low energy electron flooding for charge compensation.

Electrode Preparation

To prepare the working electrode, 2 mg of catalyst powders were ultrasonically dispersed in a mixed solution of 100 μ L Nafion (0.5 wt% in ethanol and water) for about 0.5 h. Then, 10 μ L of suspension was dropped onto a glassy carbon electrode (GCE) of 3.0 mm in diameter. The catalyst loading is 2.8 mg cm⁻². The electrode was dried for 2 h at room temperature.

To prepare the electrode for continuous water electrolysis, 36 μ L of suspension was dropped onto a 0.6 x 0.6 cm² Ni foam substrate. The catalyst loading is 2.0 mg cm⁻². The electrode was dried for 2 h at room temperature.

Electrochemical Measurements

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 on GCE. A clean platinum foil is used as counter electrode, and a saturated Ag/AgCl electrode is used as reference electrode. The electrolyte was N₂ saturated 1 M KOH solution. The linear scan voltammetry (LSV) was tested at a rate of 5 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.

Electrolysis and H₂ quantification

Water 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 is used as working electrode. A clean platinum foil is used as counter electrode. A saturated Ag/AgCl electrode is used 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.

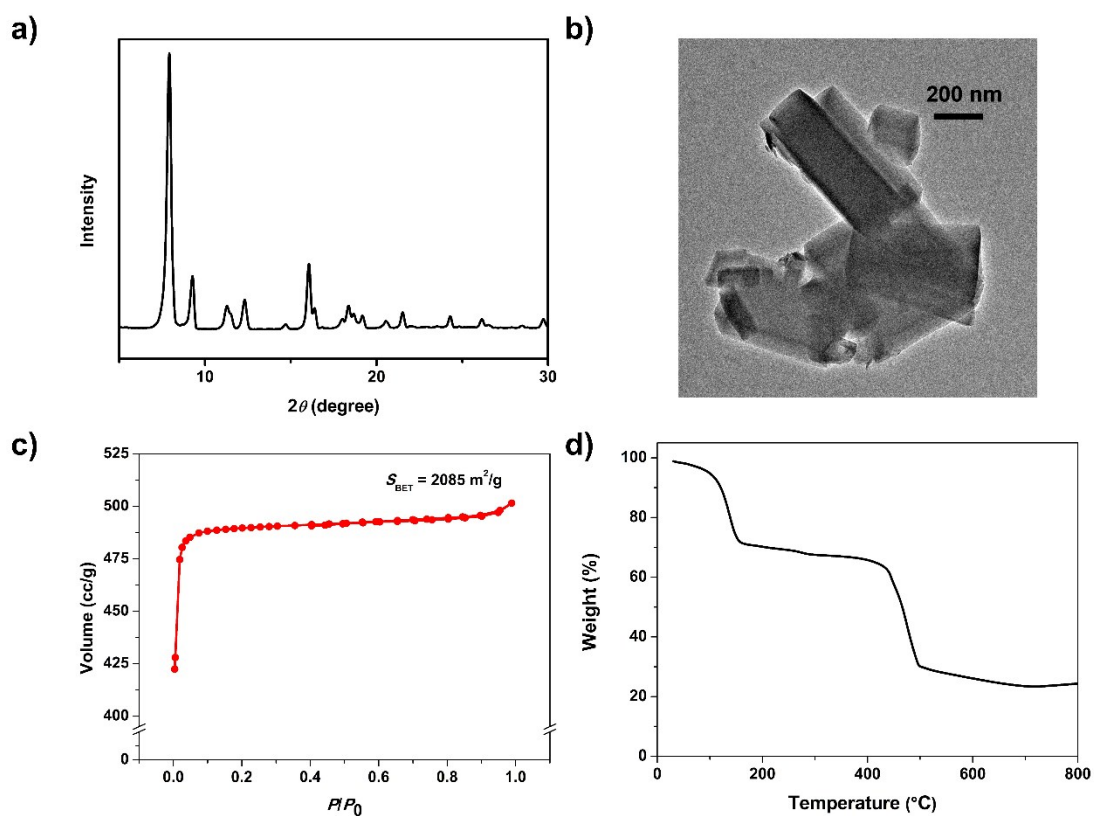


Fig. S1 Characterization of the Ni-MOF $\text{Ni}_2(\text{bdc})_2(\text{ted})$. a) the XRD pattern, b) TEM image, c) the N_2 adsorption isotherm, d) the TGA curve.

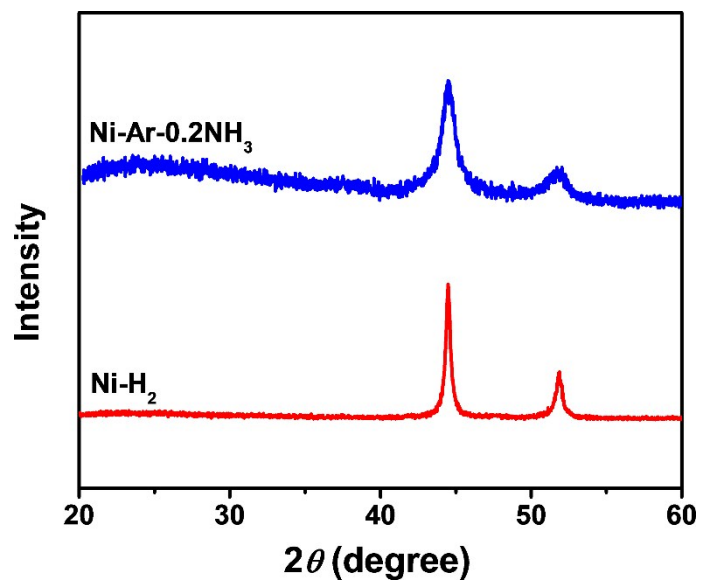


Fig. S2 XRD patterns of the sample Ni-H₂ & Ni-Ar-0.2NH₃.

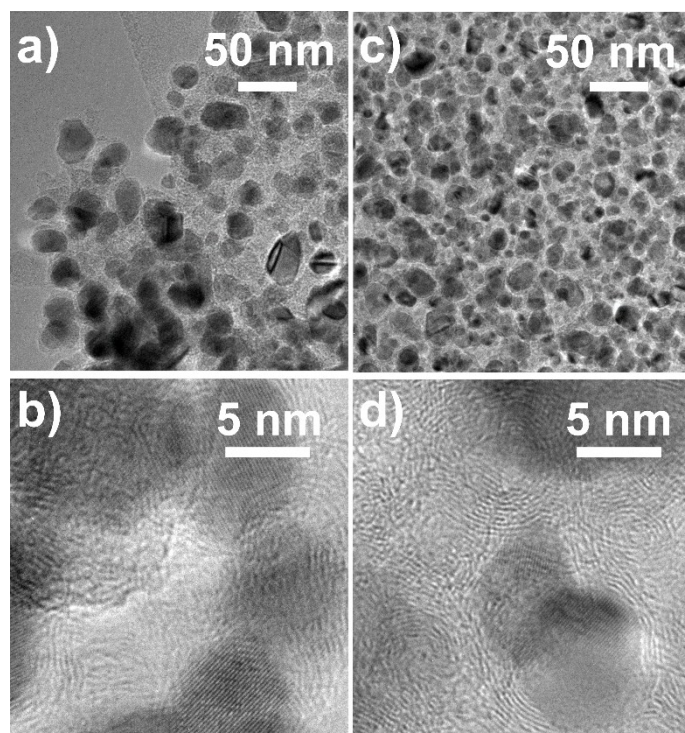


Fig. S3 TEM & HRTEM images of a, b) Ni-H₂ & c, d) Ni-Ar-0.2NH₃.

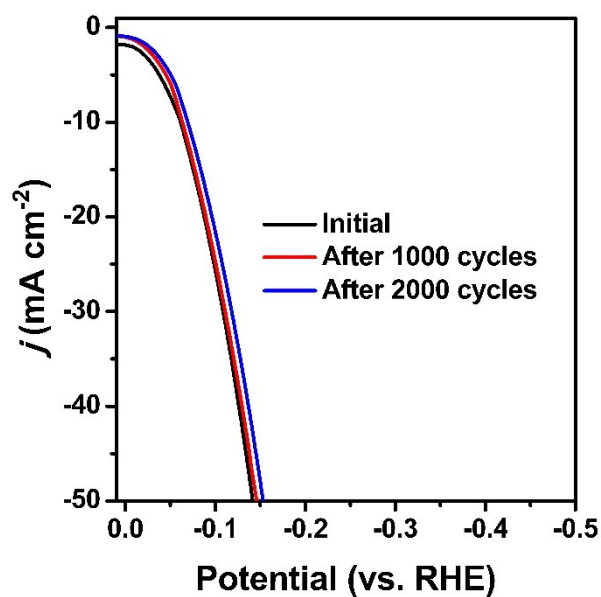


Fig. S4 polarization curves of Ni-0.2NH₃ on GCE after certain CV sweeps.

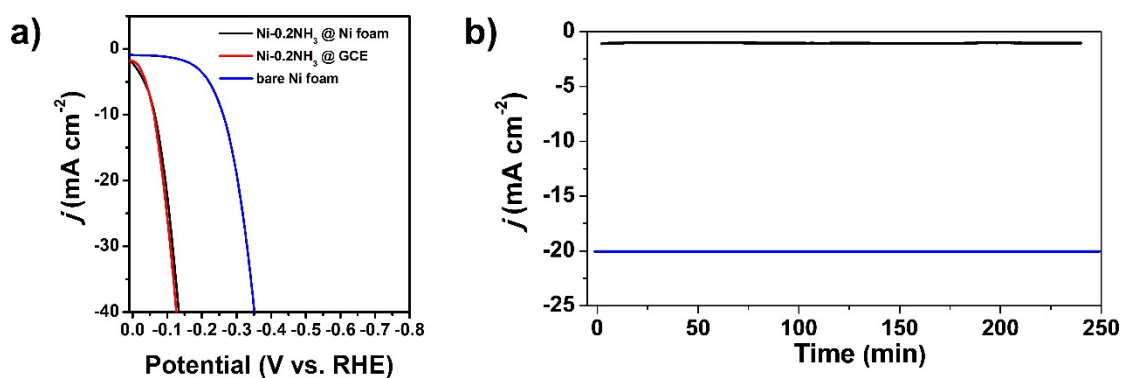


Fig. S5 a) Linear scanning voltammetry curve of Ni-0.2NH₃ on different substrate in 1M KOH solution, the performance of bare Ni foam substrate is also shown for comparison. b) Current density–time ($j-t$) curves obtained for HER in 1 M KOH solution with bare Ni foam at $\eta = 110$ mV for 4 h (black line), compared with the constant current density of 20 mA cm^{-2} of the Ni-0.2NH₃ sample in chronopotentiometry test (blue line).

Table S1 Summary of the HER catalytic activity of representative Ni-based catalysts in alkaline solutions

Catalyst	Electrolyte	Loading (mg/cm ²)	η (mV)	j (mA·cm ⁻²)	Ref.
MOF-derived Ni NPs	1M KOH	2.8	88	20	This work
			61	10	
commercial Ni wires	1M KOH	--	430	20	1
Ni nanopowders	1M KOH	1	270	20	2
Ni-Mo nanopowders	2M KOH	1	70	20	2
deposited Ni-Cu composite	1M KOH	--	200	19.3	3
Ni/NiO@ MWCNTs	1M KOH	0.28	80	10	4
		8	95	100	
Ni NPs @ MWCNTs	1M KOH	--	220	20	5
Ni ₂ P NPs	1M KOH	1	205	20	6
NiP ₂ @ carbon cloth	1M KOH	4.3	102	10	7

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