Supporting Information

Innovative Bipyridine-Bridged Metal Porphyrin Polymer for Robust and Superior Electrocatalytic Hydrogen Evolution

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Experimental section

Reagents and materials

All reagents (analytical grade) used in this study were commercially available and were employed as received without further purification, unless otherwise specified. N, N-Dimethylformamide (DMF), cobalt chloride (CoCl₂), nickel chloride (NiCl₂), methanol (CH₃OH), and potassium hydroxide (KOH) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. Deionized water, obtained from a Milli-Q Ultrapure water system, was used throughout all experiments, including the electrochemical measurements.

Material Charaterizations

The electronic structures of the materials were characterized using X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250Xi spectrometer, employing Al Kα radiation as the X-ray excitation source. The porosity of the materials was determined from adsorption-desorption data, obtained using a Micromeritics ASAP 2020 M surface area and porosity analyzer, via the Brunauer-Emmett-Teller (BET) method. Prior to measurement, the samples were degassed for 12 h at 100 °C under vacuum conditions. The morphologies and energy-dispersive spectroscopy (EDS) of the products were analyzed using a high-resolution field emission scanning electron

microscope (SEM) on a JEOL 2100 microscope. UV-vis absorption spectra were recorded with a JASCO V-570 spectrophotometer (Shimadzu) in DMSO. Fourier transform infrared (FTIR) spectra were acquired using KBr pellets on a MB154S infrared spectrometer, over the range of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹. The solid-state ¹³C NMR spectra were measured on a Bruker Avance III 400 spectrometer.

Electrochemical characterizations

All electrochemical characterizations were conducted using a CHI614E electrochemical workstation in a standard three-electrode setup. In this system, Ni foam (NF) served as the working electrode, a platinum tablet as the counter electrode, and the Hg/HgO (1.0 M KOH) as the reference electrode. To prepare the working electrode, 2 mg of the catalyst was dispersed in 0.55 mL of a 93:7 ethanol/nafion (5 wt%) solution, and 80 µL of the well-mixed suspension was drop-cast onto NF paper. The HER activity of the prepared samples was evaluated by recording linear sweep voltammetry (LSV) polarization curves in the voltage range of -0.8 to -1.6 V using 1.0 M KOH, and all HER potentials were referenced against the reversible hydrogen electrode (RHE) using the appropriate Nernst equation. The effective surface area of the samples immersed in the electrolyte was 1.0×1.0 cm². To assess the catalytic active sites and electrochemical active surface area (ECSA) of the materials, electrochemical double-layer capacitance (C_{dl}) was measured at the electrode-electrolyte interface by cyclic voltammetry (CV) at various scan rates in 1.0 M KOH. For the solution resistance, electrochemical impedance spectroscopy (EIS) was performed over a frequency range of 10⁻² to 10⁶ Hz with a potential of -1.1 V during the water splitting process. R_{ct} values are experimentally determined through EIS, modeled via equivalent circuits, and extracted from Nyquist plot fittings. The long-term stability of Bpy-CoTNPP in an alkaline solution was evaluated over 10 h, with hydrogen generation monitored by gas chromatography to calculate Faradaic efficiency.

Preparation of catalysts

The synthesis process for the electrocatalysts Bpy-CoTNPP, Bpy-NiTNPP, and Bpy-(Co-Ni)TNPP is depicted in Scheme 1. Typically, a 100 mL round-bottom flask was equipped with Bpy (7.8 mg), TNPP (100 mg), KOH (100 mg), and dry DMF (50 mL). The mixture was subjected to ultrasonication for 1 h to ensure uniform dispersion, followed by heating at 115 °C for 72 h. After the reaction, the mixture was allowed to cool to room temperature. The solvent was then removed under vacuum using a rotary evaporator. The resulting solid was filtered, washed several times with deionized water, and dried at 60 °C under vacuum for 12 h, yielding Bpy-TNPP as a black powder precursor. To synthesize Bpy-CoTNPP, Bpy-TNPP (50 mg), CoCl₂(188 mg), methanol (30 mL), and tetrahydrofuran (THF, 30 mL) were added to a 100 mL flask. The mixture was dispersed uniformly using ultrasonic treatment and then heated at 80 °C for 24 h. Upon completion of the reaction, the resulting black reaction mixture was filtered and washed several times with deionized water to remove any unreacted monomers and CoCl₂ until the filtrate was colorless. The remaining black powder was dried at room temperature for 12 h under vacuum to obtain the final product, Bpy-CoTNPP. The synthesis of Bpy-NiTNPP and Bpy-(Co-Ni)TNPP followed the same procedure as for Bpy-CoTNPP, except that CoCl₂ was replaced with NiCl₂ for Bpy-NiTNPP, and a mixture of CoCl₂ and NiCl₂ was used for Bpy-(Co-Ni)TNPP.



Figure S1. SEM image (a, the scale bar is 200 μm), elemental mapping images (b-e) and EDS image (f) of Bpy-CoTNPP.



Figure S2. SEM spectrum (a), elemental mapping images (b-e) and EDS image (f) of Bpy-CoTNPP after stability test.



Figure S3. UV-vis absorption spectra of Bpy-CoTNPP before and after stability test.



Figure S4. Cyclic voltammetry curves of the samples scanned at different rates from 20 to 100 mV s⁻¹ in 1.0 M KOH: (a) Bpy-CoTNPP, (b) Bpy-(Co-Ni)TNPP, (c) Bpy-NiTNPP, and (d) Bpy-TNPP.



Figure S5. Pore size distribution of Bpy-CoTNPP and Bpy-TNPP.

Electrocatalysts	Overpotential (mV @ 10 mA	Refs.
	cm ⁻²)	
MOF-Derived NiCo ₂ O ₄ /CeO ₂ HNPs	290 (1.0 M KOH)	[1]
V(III)-NiCo ₂ O ₄	344 (1.0 M KOH)	[2]
0.5FeNiCo ₂ O ₄ @CC	258 (1.0 M KOH)	[3]
1% P-NiCo ₂ O ₄	370 (1.0 M KOH)	[4]
MOF-Derived CuCoO ₂	364.7 (1.0 M KOH)	[5]
MOF-Derived CeO ₂ /C nanorod	297 (1.0 M KOH)	[6]
MOF-Derived Ni ₃ S ₂ /MoS ₂ hollow	303 (1.0 M KOH)	[7]
spheres		
CoZnCdCuMnS@CF	173 (1.0 M KOH)	[8]
MOF-Derived CoNiO@NCNT	315 (1.0 M KOH)	[9]
MOF-Derived Co(Zn)S ₂ /CC	248 (1.0 M KOH)	[10]
MOF-Derived CoFeP/NF	253 (1.0 M KOH)	[11]
MOF-Derived MnCo ₂ O ₄ /CeO ₂	276 (1.0 M KOH)	[12]
FeCoMo-P	273 (1.0 M KOH)	[13]
Cu-NiSe@CC	270 (1.0 M KOH)	[14]
CoPS@NPS-C	191 (1.0 M KOH)	[15]
Bpy-CoTNPP	130 (1.0 M KOH)	This work

 Table S1. Comparison of HER performance of Bpy-CoTNPP with some other reported
 electrocatalysts at 10 mA cm⁻²

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