Electronic Supplementary Information

Ultrafine NiCoP-decorated on N, S, P-codoped hierarchical porous carbon nanosheets as efficient bifunctional electrocatalyst for oxygen

reduction and oxygen evolution

Hua-Jie Niu, Ai-Jun Wang, Lu Zhang, Jing-Jing Guo, Jiu-Ju Feng *

College of Geography and Environmental Sciences, College of Chemistry and Life Sciences,

Zhejiang Normal University, Jinhua 321004, China

*Corresponding author: jjfeng@zjnu.cn (J.J. Feng).

Experimental

1. Chemicals

Thiourea, cobalt acetate (CA), nickel phthalocyanine (NiPc), phytic acid (PA), and commercial Pt/C (50 *wt%*) were supplied from Aladdin Chemical Reagent Company (Shanghai, China). The other chemicals were of analytical grade and used without further purification. All of the aqueous solutions were prepared with twicedistilled water throughout the whole experiments.

2. Characterization

The morphology and structure of the samples were characterized by scanning electron microscopy (SEM) with a Hitachi S-4800 scanning electron microanalyzer with an accelerating voltage of 15 kV, transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HR-TEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements on a JEM-2100F microscope operated at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo VG ESCALAB 250 spectrometer with an Al Ka X-ray irradiation (1486.6 eV photons) for excitation operated at 120 W. X-ray diffraction (XRD) spectra were acquired on a Philips PW3040/60 diffractometer by using Cu Ka radiation source (1 ¹/₄ 0.15405 nm). Raman spectrum was collected from a Renishaw 1000 spectrometer with a 532 nm laser excitation wavelength. Thermogravimetric analysis (TGA) was performed in air on a Netzsch STA 449 C thermogravimetric analyzer.

3. Preparation of NiCoP/NSP-HPCNS modified electrodes

For typically preparing the catalyst ink, 5 mg of the NiCoP/NSP-HPCNS sample was put into the mixture containing 500 µL of ethanol, 470 µL of water and 30 µL of Nafion (5 *wt*%). Next, the mixture was further ultrasonicated for 30 min to obtain a homogeneous suspension. Afterwards, 16 µL of the catalyst ink was dropped onto a freshly-cleaned glassy carbon rotating disk electrode (RDE, $\Phi = 5$ mm) with a catalyst loading of 0.4 mg cm⁻². In the controls, commercial Pt/C and RuO₂ catalysts modified electrodes were constructed in a similar way with the mass loading of 0.15 mg cm⁻².

4. Electrochemical experiments

Electrochemical measurements were performed on a CHI 660E electrochemical workstation (CH Instrument, Chenhua Co., Shanghai, China). A conventional threeelectrode system was adopted, including a RDE as the working electrode, a Pt wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Besides, a graphite rod was used as the counter electrode for oxygen evolution reaction (OER).

For oxygen reduction reaction (ORR), the cyclic voltammetry (CV) measurements were carried out in N_2 - or O_2 -saturated 0.1 M KOH solution with a scan rate of 50 mV s⁻¹. The ORR measurements were performed by linear sweep voltammetry (LSV) in the O_2 -saturated alkaline electrolyte with a rotation rate of 1600 rpm and a scan rate of 10 mV s⁻¹. The electrolyte was initially bubbled with O_2

for 30 min before each experiment and maintained over the electrolyte during the whole test. In order to evaluate the methanol-tolerance at a rotation rate of 1600 rpm, the chronoamperometric curves were recorded in the alkaline solution by injecting 1 M methanol at 300 s.

The OER measurements were performed in the O_2 -saturated alkaline conditions. The electrocatalytic activity was examined by LSV with a rotation rate of 1600 rpm and a scan rate of 5 mV s⁻¹. All the OER data were corrected with iR compensation.

The electrochemically active surface area (ECSA) of the NiCoP/NSP-HPCNS was evaluated from the CV curves acquired at different scan rates (5, 10, 20, 40, 60, and 80 mV s⁻¹) in the potential window of 1.049-1.149 V (*vs.* RHE). The double-layer capacitance (C_{dl}) was the slope of the linear segment in the plot of the current density (at 1.099 V *vs.* RHE) against the scan rate. The stability measurements were performed by chronopotentiometry.



Fig. S1. The particle-size distribution of NiCoP NPs.



Fig. S2. Elemental line-scanning profiles of NiCoP/NSP-HPCNS. Inset is the HAADF-STEM image.



Fig. S3. TG-DSC curves of the NiCoP/NSP-HPCNS.



Fig. S4. (A) Nitrogen adsorption-desorption isotherms and (B) pore size distribution curve of the NiCoP/NSP-HPCNS.



Fig. S5. High-resolution S 2p XPS spectrum of NiCoP/NSP-HPCNS.



Fig. S6. SEM images of the (A) NiCo/NSP-C-0.5 and (B) NiCo/NSP-C-4.



Fig. S7. SEM images of the (A) NiCo/NSP-C-700 and (B) NiCo/NSP-C-900.



Fig. S8. CV curves of the catalysts prepared at different pyrolysis temperature in 0.1 M KOH at 50 mV s⁻¹.



Fig. S9. LSV curves of the catalysts prepared at different pyrolysis temperature (A) and mass ratios of thiourea (B).



Fig. S10. (A) LSV curves of Pt/C with different rotating rates in the O_2 -saturated 0.1 M KOH electrolyte at 10 mV s⁻¹. (B) The K-L plots at different potentials.



Fig. S11. LSV curves of Pt/C before and after 2,000 cycles in the O_2 -saturated 0.1 M KOH at 10 mV s⁻¹.



Fig. S12. CV curves of NiCoP/NSP-HPCNS (A) and Pt/C (B) without and with 1.0 M methanol in the O_2 -saturated alkaline electrolyte at 50 mV s⁻¹.



Fig. S13. CV curves of NiCoP/NSP-HPCNS (A) and RuO_2 (B) acquired in 1 M KOH at different scan rates. (C) The C_{dl} values.

Table S1. Comparison of the ORR data in 0.1 M KOH with other non-precious metal

 based catalysts reported previously.

Catalysts	Loading (mg cm ⁻²)	E _{onset} (V vs. RHE)	<i>E</i> _{1/2} (V <i>vs</i> . RHE)	п	references
NiCoP/NSP-HPCNS	0.4	0.92	0.84	4	This work
Fe-N-HPC-AH	0.38	0.97	0.87		1
Fe/Co-CNTs-800	0.5	0.928	0.783	3.9	2
S-Co _{9-x} Fe _x S ₈ @rGO	0.5	0.94	0.84	3.97	3
Co/Co _x S _y @S, N- codoped carbon fibers	0.4	0.83	0.74	3.97	4
NiCo/porous fibrous carbon	0.13	0.92	0.79	3.89	5
CoNP@N-C/N-graphene	0.24	0.9	0.83	3.8	6
NiCo ₂ S ₄ /N-CNTs	0.25	0.93	0.8	3.82	7
S, N-Fe/N/C-CNTs	0.25	_	0.85	4	8
NiFe/Co, N-codoped carbon nanoframes	0.12	0.893	0.79	3.89	9
Co-N _x /C nanorod array	0.5	_	0.87	3.98	10

Note: CNTs (carbon nanotubes)

Catalysts	Overpotential (mV @ j=10 mA cm ⁻²)	Tafel slopes (mV dec ⁻¹)	References
NiCoP/NSP-HPCNS	299	71.1	This work
CoP@N-doped porous carbon spheres	350	103	11
CoP/N-carbon nanotube hollow polyhedron	310	70	12
NiCoP/C nanoboxes	330	96	13
NiFeP@3D-FeNC	250	65	14
Co ₄ N/carbon fibers network/carbon cloths	310	81	15
N-CNT/CoFe-CoFe ₂ O ₄	310	63	16
NiO/CoN porous nanowires	300	35	17
NiFe/N-C	330	45	18
CoPS@NSP-C	320	98	19
NiCo ₂ P _x /CNTs	284	50	20

Table S2. Comparison of the OER data in 1 M KOH with non-precious metal-based

 catalysts in the literature.

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