

Porous Cobalt Phosphide/Graphitic Carbon Polyhedra Hybrid Composites for Efficient Oxygen Evolution Reactions

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Experimental Section

Preparation of ZIFs template. All chemicals and solvents were purchased from commercial sources and used without any further purification. In a typical preparation, 5 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 40 ml methanol to form a clear solution, which was then poured into 40 ml of methanol containing 20 mmol 2-methylimidazole. After thorough mixing and incubation at room temperature for 24 h, the resulting pink precipitates were collected by centrifugation, washed with ethanol several times and finally dried in air at 60°C .

Synthesis of CoP@GC hybrid composites and CoP particles. In a typical procedure, 200 mg ZIF-67 and 100 mg red phosphorus were placed at two separate positions in a combustion boat and then heated then heated to 700°C at a rate of 2°C min^{-1} and maintained at this temperature for 2 h under an argon gas flow of 60 mL min^{-1} . CoP particles were prepared through phosphorization of commercial Co_3O_4 particles according to previously reported method [S1].

Characterization. X-ray diffraction (XRD) patterns were collected on a Bruker D8-Advance using Cu K_α radiation ($\lambda=1.5406\text{ \AA}$). Field-emission scanning electron microscopy (FESEM) images were recorded on a JSOL JSM-7600F scanning electron microscope. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), high-angle dark-field scanning TEM (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) elemental mapping images were all recorded on a JEOL JEM-2100F transmission electron microscope. The X-ray photoelectron spectroscopy (XPS) analyses were performed using a PHI 5600 XPS instrument. The Brunauer-Emmett-Teller (BET) specific surface areas of products were

calculated from the results of N₂ physisorption at 77 K using a Quantachrome Instruments Autosorb AS-6B instrument.

Electrocatalytic measurements. All electrochemical measurements were performed in a three-electrode glass cell system including platinum foil and Ag/AgCl (saturated KCl) electrodes as the counter and the reference electrodes, respectively, and a glassy carbon electrode (GCE, 5 mm in diameter) coated with as-prepared samples as the working electrode. To prepare the working electrode, 5 mg of the sample was dispersed in 1 ml water/ethanol mixed solvent (v/v=1:1) solution with 40 μ L of 5 wt% Nafion and then sonicated for 30 min to form a homogenous catalyst inks. After that, 10 μ L of the catalyst ink was dropped onto the surface of the pre-polished GCE. For comparison, a bare GCE that had been polished and cleaned was also evaluated for electrochemical measurements. Before the measurement, the electrolyte (1 M KOH solution) was purged by O₂ for at least 30 min to ensure the saturation of the electrolyte. Linear sweep voltammetry (LSV) curves were measured at a sweep rate of 2 mV s⁻¹ to obtain the polarization curves. The accelerated durability tests were conducted by potential cycling for 1000 cycles and at 347 mV in 1 M KOH solution for 10 h. All potentials reported here were referenced to the reversible hydrogen electrode (RHE) through RHE calibration. Electrical impedance spectroscopy (EIS) was carried out from 10⁶ to 0.1 Hz with an AC amplitude 5 mV.

S2

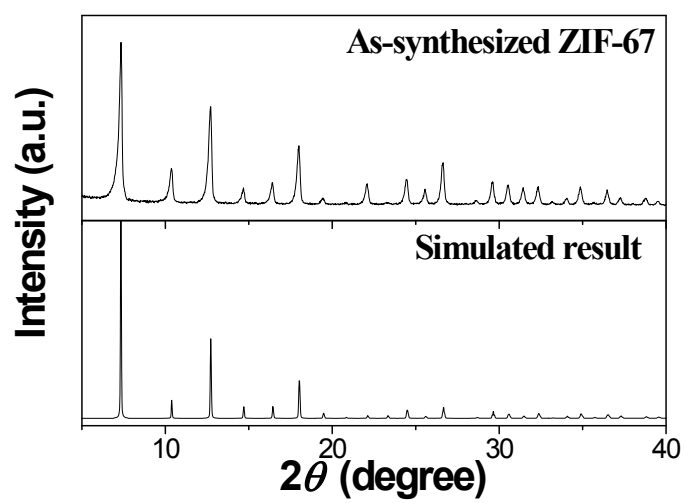


Figure S1. Experimental and simulated XRD patterns of ZIF-67.

S3

Table S1 Comparison of the OER activities of the CoP catalysts in alkaline conditions with recently reported Co-based Catalyst.

Electrocatalyst	Overpotential at 10 mA cm ⁻²	Electrolyte	References
CoP hollow polyhedron	400 mV	1 M KOH	S1
(Co _x Fe _{1-x}) ₂ P nanourchins	370 mV	0.1 M KOH	S2
CoCr ₂ O ₄ /carbon nanosheets	365 mV	1 M KOH	S3
Ni-modified CoP-based nanoparticles	360 mV	1 M KOH	S4
CoO _x -C	360 mV	0.1 M KOH	S5
Mesoporous cobalt phosphate	380 mV	1 M KOH	S6
Zn ₂ Co ₂ O ₄	390 mV	1 M KOH	S7
NiCo ₂ O ₄ Nanoneedles	565 mV	1 M KOH	S8
CoP/graphene oxide	340 mV	1 M KOH	S9
NiCo double hydroxide nanosheets	367 mV	1 M KOH	S10
CoP@GC (This work)	345 mV	1 M KOH	This work

All potentials were converted to the reversible hydrogen electrode (RHE) scale, unless otherwise stated.

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