

Supporting Information

Interface engineering in α -Co(OH)₂/ZIF-67 heterostructure for enhanced oxygen evolution electrocatalysis

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EXPERIMENTAL SECTION

Materials. All commercially available chemical materials, including $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2-methylimidazole (2-MIM), Hexamethylenetetramine (HMT), KOH (85%), Nafion solution (5 wt%, Aldrich corporation), and carbon paper in this experiment were not subjected to special treatment prior to use.

Synthesis of $\alpha\text{-Co}(\text{OH})_2$ nanosheets

In a typical synthesis of $\alpha\text{-Co}(\text{OH})_2$ nanosheets, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (6 mmol) and HMT (24 mmol) were dissolved in deionized water (30 mL). Then, the resulting homogeneous solution was transferred to an autoclave lined with polytetrafluoroethylene, with a volumetric capacity of 50 mL. The autoclave was sealed and heated at a temperature of 110 °C for 8 hours, and then naturally cooled to room temperature. The collected $\alpha\text{-Co}(\text{OH})_2$ product was washed twice with deionized water and once with ethanol, and then dried at 60 °C for 6 hours.

Synthesis of $\alpha\text{-Co}(\text{OH})_2/\text{ZIF-67}$ heterostructures

The $\alpha\text{-Co}(\text{OH})_2/\text{ZIF-67}$ heterostructures were prepared according to the following procedure. The as-synthesized $\alpha\text{-Co}(\text{OH})_2$ powder (50 mg) was dispersed in anhydrous methanol (10 mL) to suspension A. Then, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.6 mmol) and 2-MIM (200 mg) were dissolved in anhydrous methanol (10 mL) to form clear solution B and solution C, respectively. The solution B was quickly poured into suspension A under vigorous stirring for 10 minutes. Then solution C was poured into the above mixture and continuously stirred for 4 h. It was centrifuged, washed with

ethanol and then dried at 60 °C for 6 hours, generating the α -Co(OH)₂/ZIF-67-0.6 product. Other heterostructures including α -Co(OH)₂/ZIF-67-0.4, -0.5, -0.7 were prepared under the identical procedure except that different quantities (0.4, 0.5 and 0.7 mmol) of Co(NO₃)₂·6H₂O were used.

Synthesis of ZIF-67 nanoparticle

The preparation of bare ZIF-67 nanoparticle is similar to the procedure of α -Co(OH)₂/ZIF-67-0.6 heterostructures, except that α -Co(OH)₂ nanosheets were not included.

Synthesis of ZIF-67(100 nm) and characterization

Co(NO₃)₂·H₂O (150 mg) was dissolved in water (23 mL) to form solution A. 2-MIM (1800 mg) was dissolved in water (9 mL) to form solution B. And CTAB (100 mg) was dissolved in water (20 mL) to form solution C. Solution B was quickly poured into solution A, and then solution C was added. Further, it was continuously stirred for 6 h, then centrifuged, washed with ethanol and dried. This sample was characterized by SEM with cubic shape and about 100 nm in size, which is denoted as ZIF-67(100 nm) (Fig. S1c).

Material Characterizations.

Field emission scanning electron microscopy (FESEM) measurements were recorded on a FEI Nova NanoSEM 450 field emission scanning electron microscope at an accelerating voltage of 18 kV. Transmission electron microscopy (TEM) images were

collected on a transmission electron microscope of Tecnai-G2 F30 produced by FEI Company with the operating voltage of 300 kV. And the energy dispersive X-ray spectrometry (EDS) was measured by the attachment on the TEM microscope. The XRD-7000S model X-ray powder diffractometer (Cu-K α 1 radiation source, wavelength $\lambda = 1.5406 \text{ \AA}$) produced by Shimadzu Corporation was applied with the scanning speed of 5° min^{-1} . The X-ray photoelectron spectroscopy (XPS) was performed using ESCALABTM 250Xi equipment with an Al K α X-ray radiation source for excitation.

Electrocatalytic Measurements. The typical three-electrode system was applied to evaluate the OER catalytic performances using the CHI660E electrochemical workstation (Chenhua, Shanghai). And KOH (1 M) was used as electrolyte throughout. During the electrochemical test, a standard three-electrode system is used: glassy carbon electrode as working electrode, Pt plate as counter electrode, and Hg/HgO electrode as reference electrode. For working electrode preparation, each as-prepared sample (4 mg) was dispersed in 480 μL H₂O, 480 μL ethanol and 40 μL Nafion solution (5 wt%). Then the suspension was ultrasonically treated and mixed uniformly to obtain a catalyst ink. The evenly mixed ink (16 μL) was dropped on the pre-polished glassy carbon electrode with a diameter of 5 mm, and dried under ambient conditions with loading amount of 0.326 mg/cm². The potential reported in this study was converted with respect to a reversible hydrogen electrode (RHE)

according to the following equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.0591 \cdot \text{pH} + 0.098 \text{ V}$ (pH = 13.98). Furthermore, the overpotential (V) was calculated ($\eta = E_{\text{RHE}} - 1.23 \text{ V}$). Linear sweep voltammetry (LSV) was performed at a sweep rate of 5 mV s^{-1} (without IR compensation). The Tafel curve can be obtained through LSV data conversion, the potential (vs. RHE) as the ordinate and the logarithmic value of the current density as the abscissa. The linear part fitting gave the Tafel slope value. Electrochemical impedance spectroscopy (EIS) was recorded at an overpotential (320 mV) with the applied frequency range of 0.01-10⁵ Hz (AC amplitude: 5 mV). Cyclic voltammetry (CV) curves at various scan rate of 20 - 100 mV s^{-1} measured in the potential range of 0.3 – 0.4 V versus Hg/HgO were plotted and extracted to calculate the double layer capacitance (C_{dl}). The long-term stability of the electrode was tested by loading the $\alpha\text{-Co(OH)}_2/\text{ZIF-67-0.6}$ catalyst (1 mg cm^{-2}) on carbon fiber paper via chronoamperometry. Turnover frequencies (TOFs) for the OER are calculated using the following equation:

$$\text{TOF} = jS/4Fn$$

where j (A cm^{-2}) is the current density, S is the surface area (1.963 cm^2), the number 4 means 4 electron transfer in the OER reaction, F is the Faraday constant of $96485 \text{ C} \cdot \text{mol}^{-1}$, and n is the total metal ion molar number from the EDS results of ZIF-67, $\alpha\text{-Co(OH)}_2/\text{ZIF-67-0.6}$ and $\alpha\text{-Co(OH)}_2$. Assuming that Co ions were catalytically active, the TOF values of ZIF-67, $\alpha\text{-Co(OH)}_2/\text{ZIF-67-0.6}$ and $\alpha\text{-Co(OH)}_2$ were calculated.

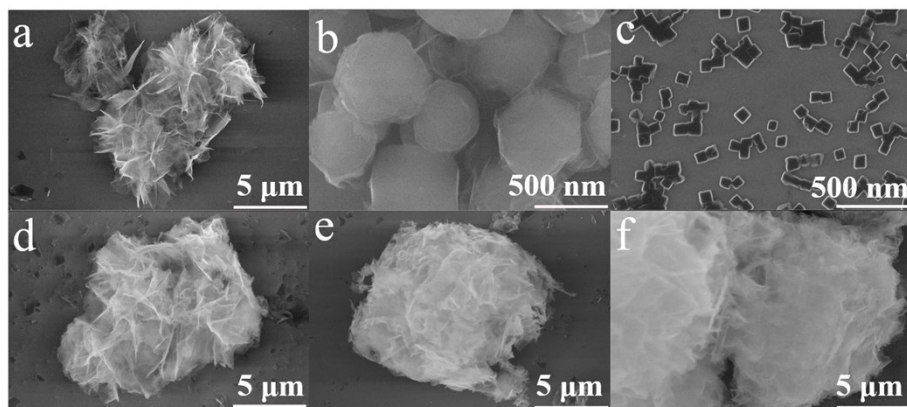


Fig S1. SEM images of (a) α -Co(OH)₂, (b) ZIF-67, (c) ZIF-67(100 nm) synthesized by other condition, (d) α -Co(OH)₂/ZIF-67-0.4, (e) α -Co(OH)₂/ZIF-67-0.5, (f) α -Co(OH)₂/ZIF-67-0.7.

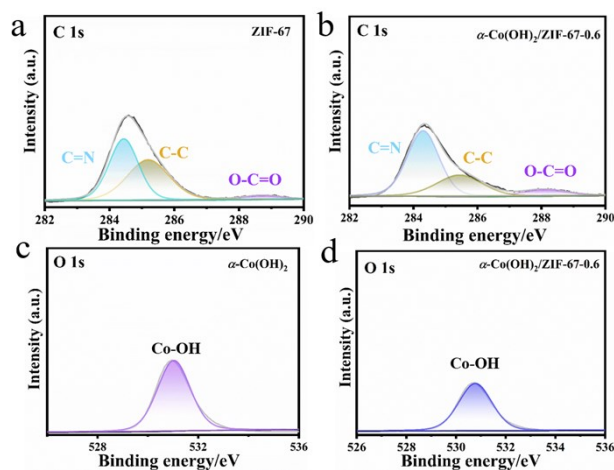


Fig S2. High-resolution XPS spectra of ZIF-67, α -Co(OH)₂ and α -Co(OH)₂/ZIF-67-0.6: (a, b) C 1s, (c, d) O 1s

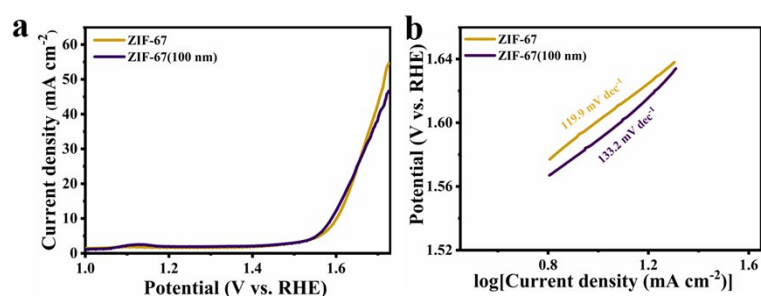


Fig S3. Electrocatalytic performances of ZIF-67 and ZIF-67(100 nm): (a) LSV polarization curves and (b) Tafel curves.

The electrochemical results indicate that the bare ZIF-67 samples with 100 nm and 500 nm show similar activity (LSV curve in Fig. S3a) and Tafel slope (LSV curve in

Fig. S3b). Thus, it further confirms that the heterostructure exhibits superior electrocatalytic performance to bare ZIF-67.

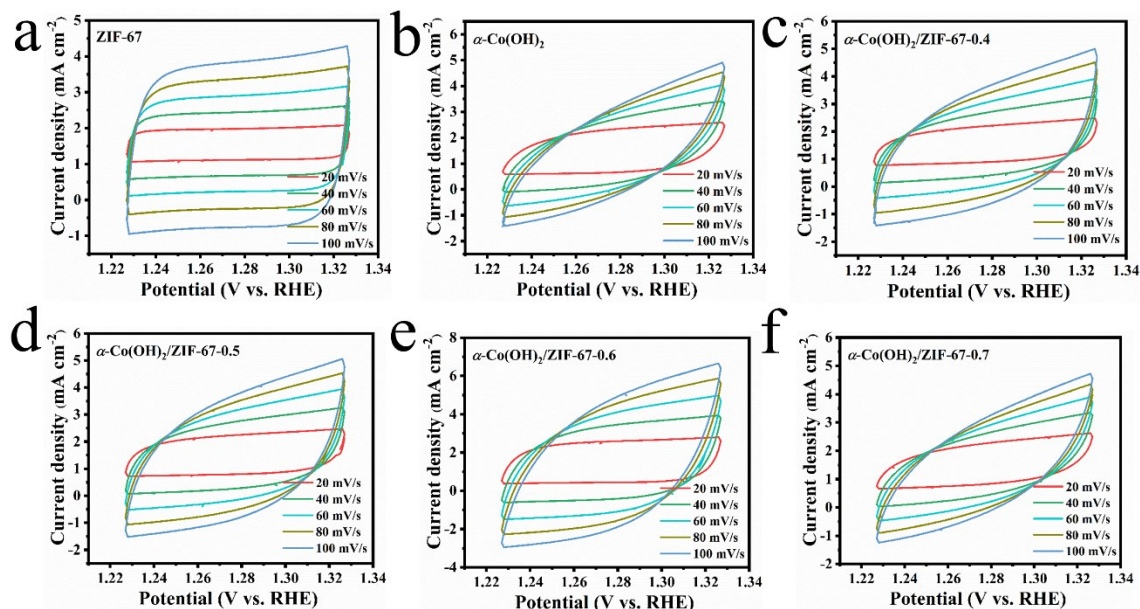


Fig S4. CV curves of ZIF-67, α -Co(OH)₂, α -Co(OH)₂/ZIF-67-0.4, α -Co(OH)₂/ZIF-67-0.5, α -Co(OH)₂/ZIF-67-0.6 and α -Co(OH)₂/ZIF-67-0.7 vs RHE at different scan rates in 1.0 M KOH aqueous solution

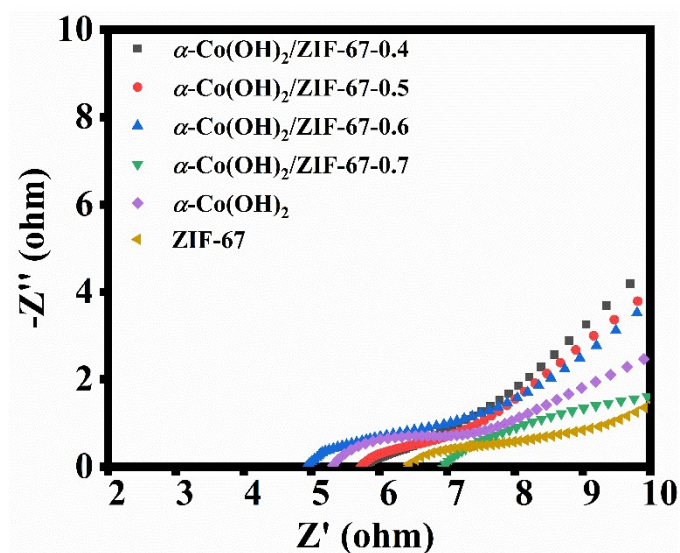


Fig S5. The local amplification of EIS Nyquist plots.

Table S1. Comparison for OER activity of α -Co(OH)₂/ZIF-67-0.6 with other electrocatalysts in 1 M KOH.

| Catalyst | Overpotential η [mV] at 10 mA cm ⁻² | Tafel slope [mV decade ⁻¹] | Ref |
|---|--|---|--|
| α -Co(OH) ₂ /ZIF-67-0.6 | 320 | 109.3 | This work |
| Ni-BDC@NiFe-LDH-2 | 272 | 45 | CrystEngComm, 2021, 23, 1172 |
| Fe-Ni LDH/MOF-b2 | 255 | 24 | Nanoscale, 2020, 12, 14514 |
| NiFe-LDH/ZIF-67 | 222 | 53 | Int J. Hydrogen Energy, 2020, 45, 1948-1958 |
| β -Ni(OH) ₂ /Ni-MOF(NF) | 292 | 44 | Inorg. Chem., 2020, 59, 7, 4764-4771 |
| Fe(OH) ₃ @Co-MOF-74(CP) | 267 | 56 | ChemSusChem., 2019, 12, 4623-4628 |
| Co(OH) ₂ /Co-MOF(CC) | 225 | 107 | Chem. Eng.J., 2021, 408, 127319 |
| ZIF-67@Co(OH) ₂ | 354 | 73.7 | J. Colloid Interf. Sci., 2020, 562, 279-286 |
| CoS _x /Co-MOF(NF) | 280 | 83 | Inorg. Chem. Front., 2020, 7, 2602-2610 |
| Ni-BDC@NiS(NF) | 330(20 mA cm ⁻²) | 63.2 | ACS Appl. Mater. Interface, 2019, 11, 44, 41595-41601. |
| Ni-MOF/LDH/NF | 220 | 36 | Appl. Catal. B Environ., 2021, 286, 5, 119906 |
| ZIF@LDH/NF | 318 | 97 | ACS Appl. Mater. Interfaces 2017, 9, 36762-36771 |
| ZIF-67/CoNiAl-LDH/NF | 303 | 88 | Electrochimica Acta 2019, 307, 275-284 |
| NiCo LDH@ZIF-67-V _O /NF | 290 | 58 | J. Mater. Chem. A, 2019, 7, 4950 |
| Co-LDH@ZIF-67(CC) | 187 | 59 | Adv. Sci. 2020, 2002631 |
| Ce-NiBDC/OG | 265 | 46 | Mater. Horiz., 2021, 8, 556-564 |
| Ni _{0.5} Co _{1.5} -bpy(PyM) | 256 | 81.8 | Sci. China Mater. 2021, 64, 137-148 |

Table S2. Data for TOF calculation.

| | ZIF-67 | α -Co(OH) ₂ /ZIF-67-0.6 | α -Co(OH) ₂ |
|--|--------------------------|---|-------------------------------|
| Weight%(Co) from EDX | 11.14 | 26.25 | 34.15 |
| $n(\text{Co})/\text{mol}$ | 0.12084×10^{-6} | 0.2847×10^{-6} | 0.37×10^{-6} |
| $j@350\text{mV}/\text{mA}/\text{cm}^2$ | 6.73 | 18.13 | 7.55 |