Electronic Supplementary Information

$CoNi_2S_4$@CoNi-LDH heterojunction grown on SSM as highly-efficient trifunctional catalyst for water-splitting and Zn-air battery

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1. Material and experimental instruments

1.1 Materials used in the experiment

Pt/C (20 wt%) was obtained from Macklin Ltd. (Shanghai, China). RuO_2 was synthesized from ruthenium chloride hydrate ($RuCl_3 \cdot 3H_2O$) purchased from Beijing Chemical Reagents Company.[1] (Beijing, China). Stain steel mash (SSM) was provided by the Hao Ke Technology Co. Ltd. (Beijing, China). KOH, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, urea and other chemicals are supplied by the Beijing Chemical Reagents Company.

1.2 Experimental Section

1.2.1 Characterizations

X-ray diffraction (XRD) experiment was tested on a Rigaku D-Max 2550 diffractometer with Cu-Kα radiation (λ = 1.5418 Å). Scanning electron microscope (SEM) and energy dispersive X-ray (EDX) spectroscopy images were obtained on a JEOL-6700 scanning electron microscope. X-ray photoelectron spectra (XPS) analysis was performed on a VG Scienta R3000 spectrometer with Al Kα (1486.6 eV) as the X-ray source. Tranmission electron microscope (TEM), high resolution TEM (HRTEM) images were obtained with microscopy of Philips-FEI Tecnai G2S-Twin, equipped with a field emission gun operating at 200 kV.

1.2.2 Electrochemical measurements

The electrochemical measurements were conducted using the three-electrode system with the electrochemical workstation (CHI 760e). The as-prepared electrodes were directly used as the work electrodes; meanwhile, graphite rod and Hg/HgO electrode were served as counter and reference electrodes, respectively. 1.0 M KOH solution and 0.1 M KOH solution was used as electrolyte for OER and ORR devices. Potentials were normalized versus the standard hydrogen electrode (RHE) according to formula below:

$$E(RHE) = E(Hg/HgO) + 0.098V + 0.591pH$$

Here, "E(Hg/HgO)" is the potential we directly measured during the experiment. For that we applied the 1.0 M KOH throughout the OER test, pH = 14; we applied 0.1 M KOH throughout the ORR test, pH = 13.

Polarization curves were performed via sweeping potentials at a scan rate of 2.0 $mV \cdot s^{-1}$ and without further IR rectification. Corresponding stabilities were examined through current-time curves at the constant potentials.

The data of Tafel slope can be plotted by the gained linear sweep voltammetry (LSV) curves, which is obtained from the follow equation:

$$\eta = a + b \log j$$

Where, "η" refers to the overpotential; "j" is the current density; "a" relates to the j_0 (exchange current density) and can be reflected by the intercept; "b" is the Tafel slope we need to acquire.

The electrochemical surface area (ECSA) is calculated by the formula below:

$$ECSA = A * C_{dl} / C_s$$

Where "A" refers to the area of the working electrode, and we set the electrode area to 0.25 cm^2 throughout the electrocatalytic testing; "C_s" relates to the electrolyte and C_s = 0.04 $mF \cdot cm^{-2}$, "C_{dl}" is the abbreviation of double layer capacitance and calculated from a series of CV curves that tested within the non-Faraday potential range (0.9254-1.0254 V vs. RHE), scan rate changed from 10 to 100 $mV \cdot s^{-1}$, increased with 10 $mV \cdot s^{-1}$ each time.

Electrochemical impedance spectroscopy (EIS) measurements are also performed with the three-electrode cell system in 1.0 M KOH, and the frequency range is from 0.1 Hz to 10 KHz, the amplitude is 5 mV.

1.2.3 Assembly and Testing of the Zn-Air Battery

As for the liquid Zn-air battery, in order to avoid electrolyte leakage, we physically compounded the SSM-based catalyst with the waterproof/breathable carbon film, and then assembled the complex as the air-cathode of the Zn-air battery.[1] In this work, we respectively adopt CoNi-LDH/SSM, $CoNi_2S_4$@CoNi-LDH/SSM and Pt/C+RuO_2/SSM electrodes as air-cathodes, zinc sheets were used as metal-anode to assemble water-based Zn-air batteries. Wherein, the applied electrolyte is the mixture of 6.0 M KOH and 0.02 M $Zn(CH_3COOH)_2$.

Both the charge and discharge curves were measured by the CHI 760e, the power density was calculated from the data of the discharge curve. Charge-discharge curves at current density of 5 $mA·cm^{-2}$ in this work were measured by the Land battery test system.

Related Figures and Tables:

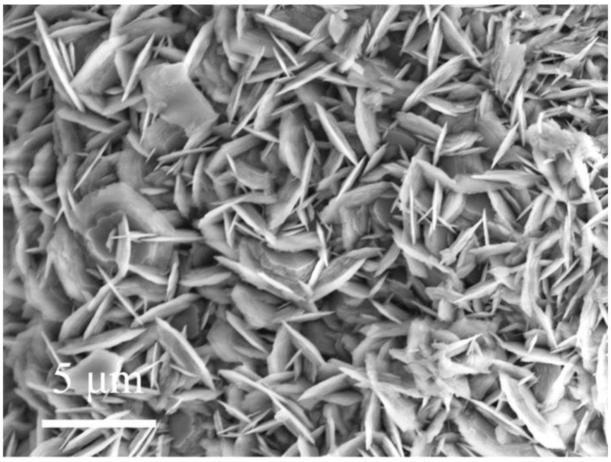

Fig. S1. SEM image of CoNi-LDH/SSM.

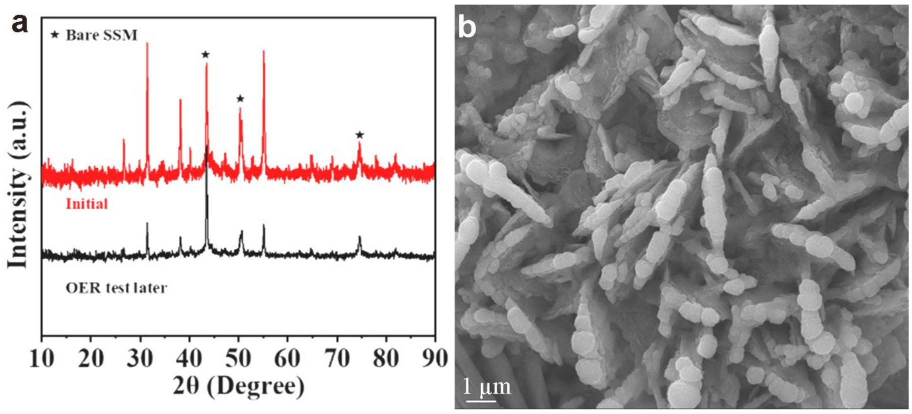

Fig. S2. (a) XRD and (b) SEM image of $CoNi_2S_4$@CoNi-LDH/SSM after i-t test for OER.

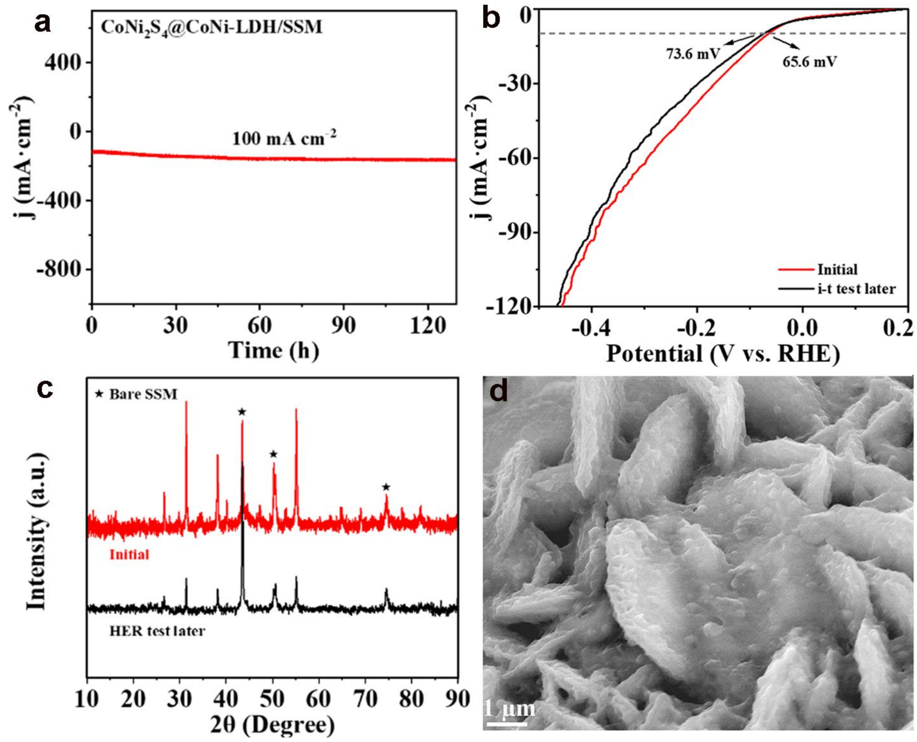

Fig. S3. The (a) i-t curves of $CoNi_2S_4$@CoNi-LDH/SSM that when the provided potential is -0.416 V. (b) LSV curves that before and after the i-t testing and corresponding (c) XRD and (d) SEM image that the i-t test later for HER.

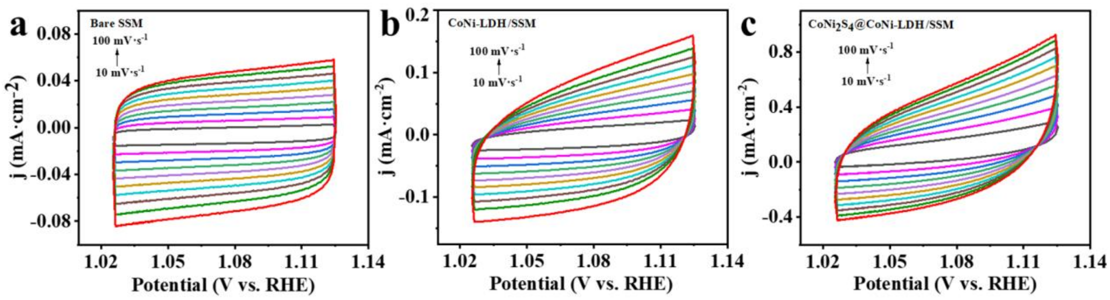

Fig. S4. The CV curves at different scan rate of (a) bare SSM, (b) CoNi-LDH/SSM and (c) $CoNi_2S_4$@CoNi-LDH/SSM.

Table S1. C_{dl}, C_s and calculated ECSA data of the related catalysts.

	C_{dl} (mF·cm^{-2})	C_s (mF·cm^{-2})	ECSA (cm^2)
$CoNi_2S_4$@CoNi-LDH/SSM	2.07	0.04	12.94
CoNi-LDH/SSM	0.44	0.04	2.75
Bare SSM	0.26	0.04	1.66

Table S2. R_s and R_{ct} data of the related samples.

	R_s (Ω)	**R_{ct} (Ω)**
$CoNi_2S_4$@CoNi-LDH/SSM	1.90	0.46
CoNi-LDH/SSM	1.90	1.42
Bare SSM	1.90	10.13

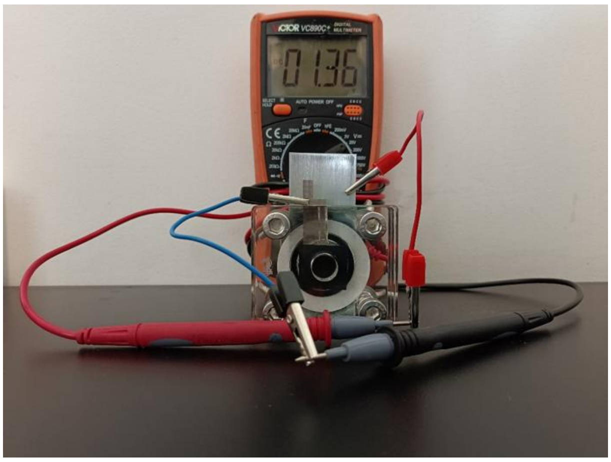

Fig. S5. The open circuit potential of the ZAB that assembled using the as synthesized $CoNi_2S_4$@CoNi-LDH/SSM applied for air-cathode.

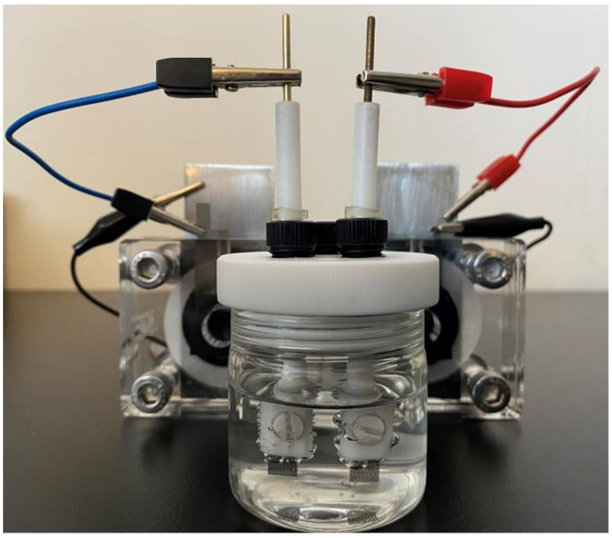

Fig. S6. Actual photogragh of the self-powered electrocatalytic water-splitting device that assembled by two ZABs using $CoNi_2S_4$@CoNi-LDH/SSM directly as the air cathode.

Reference

(1) Jian, J.; Nie, P.; Wang, Z.; Qiao, Y.; Wang, H. R.; Zhang, C. Y.; Xue, X. X.; Fang, L.; Chang, L. M. V^{5+}-Doped Potassium Ferrite as an Efficient Trifunctional Catalyst for Large-Current-Density Water Splitting and Long-Life Rechargeable Zn-Air Battery, ACS Appl. Mater. Interfaces. 2022, 14 (32), 36721-36730.