In-situ Reconstructed Amorphous MOOH Enhanced NiCoP@NiFe-LDH Bifunctional Electrocatalyst for Long Durable Seawater Electrolysis

Huiya Zhou[1,2#], Songlin Xu[1,2#], Boyao Zhang[1], Xin Li[1], Zihan Lv[1], Depeng Zhao[1,2*], Rong-Da Zhao[1,2*]

[1]School of New Energy, Shenyang Institute of Engineering, Shenyang, Liaoning, 110136, P. R. China

[2]School of Materials Science and Engineering, Liaoning University of Technology, Jinzhou, Liaoning 121000, P. R. China

Correspondences should be addressed: hellodepeng@163.com; rongdazhaoln@126.com;

1. Synthesis of NiCoP@NiFe-LDH Heterojunction Catalyst

1 mmol $Ni(NO_3)_2 \cdot 6H_2O$, 2 mmol $Co(NO_3)_2 \cdot 6H_2O$, 4 mmol NH_4F, and 9 mmol urea in 60 mL DI water under magnetic stirring (1 h, RT). The pretreated Ni foam was vertically immersed in the solution and hydrothermally reacted in a Teflon-lined stainless steel autoclave at 130°C for 5 h. After cooling to RT, the sample was rinsed three times with anhydrous ethanol and DI water, followed by drying at 60°C for 6 h to obtain the NiCo precursor-loaded Ni foam. Then, the NiCo precursor-loaded Ni foam was placed in a tube furnace for phosphorization. 0.5 g NaH_2PO_2 was positioned upstream in the quartz tube, while the sample was placed downstream. After three vacuum-argon purge cycles, the system was heated to 350°C for 120 min under high-purity argon. The as-obtained sample was named as NiCoP catalysts. Finally, 0.8 mmol $Fe(NO_3)_3 \cdot 9H_2O$, 3.2 mmol $Ni(NO_3)_2 \cdot 6H_2O$, 16 mmol urea, and 8 mmol NH_4F in 60 mL DI water. The NiCoP sample was transferred into the above solution and hydrothermally reacted at 120°C for 12 h. Post-reaction, the composite was washed with ethanol and DI water, and then dried at 60°C for 2h.

2. Materials characterization.

The crystal structure and phase composition of the samples were analyzed using an X-ray diffractometer (XRD, D/max-2500/PC) with Cu-Kα radiation. The XRD measurements were conducted at an accel-erating voltage of 100 kV, a tube current of 40 mA, a scanning range from 0° to 90°, and a scanning speed of 8° per minute. Elemental composition and valence states were determined via X-ray photoelectron spectroscopy (XPS, ESCALAB250). The microstructures of the samples were

examined with field emission scanning electron microscopy (SEM, Zeiss-Sigma 500), and the transmission electron microscopy (TEM, JEM2100F) was used to further investigate the microstructure.

3. Electrochemical measurements.

All electrochemical measurements were carried out on a CHI660 electrochemical workstation in 1 M KOH and 1 M KOH + seawater solution. The electrochemical performance and characterization of as-prepared electrodes were tested in a three-electrode system, together with a Hg/HgO electrode as reference electrode and carbon rod as counter electrode. The activity of the electrodes was evaluated by linear sweep voltammetry (LSV) curves with 90% IR compensation. Cyclic voltammetry (CV) curves were recorded at the scan rates of 1 ~ 5 and 10 mV s^{-1} to obtain the double-layer capacitance values. Electrochemical impedance spectroscopy (EIS) was measured from 0.1 Hz to 1000 kHz. The stability of the electrode was studied in a constant potential of -0.1 V vs. RHE. All the potentials were converted to RHE by Nernst equation (E_{RHE} = $E_{Hg/HgO}$ + 0.0591pH + 0.098). the values of 1 M KOH and 1 M KOH + seawater are 13.6 and 13.51, respectively.

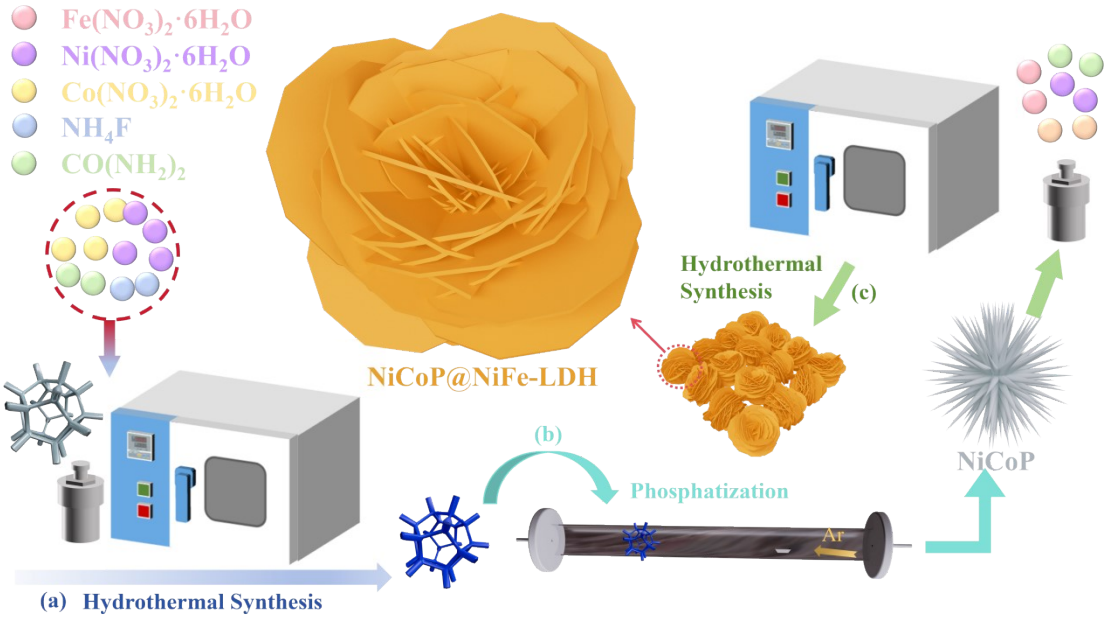

Fig. S1 (a-c) Schematic illustration of the synthesis process for NiCoP@NiFe-LDH samples

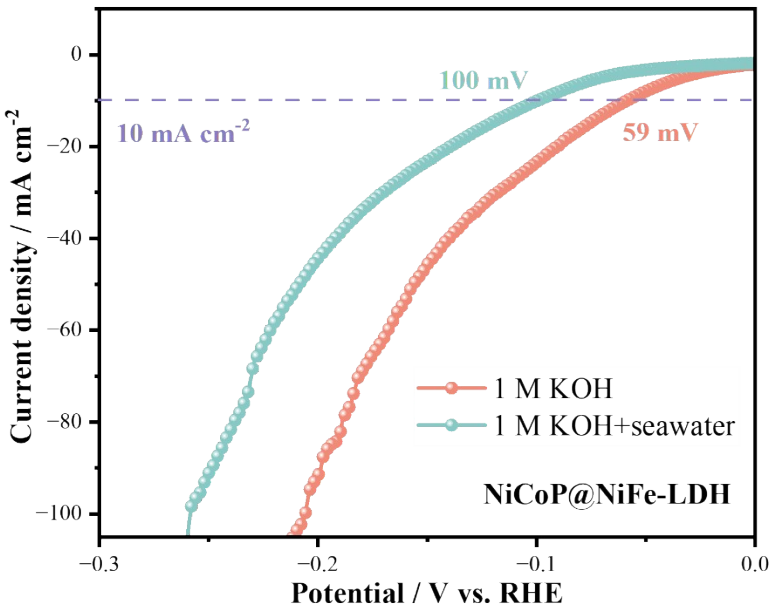

Fig. S2 HER Polarization curves of NiCoP@NiFe-LDH in different electrolytes.

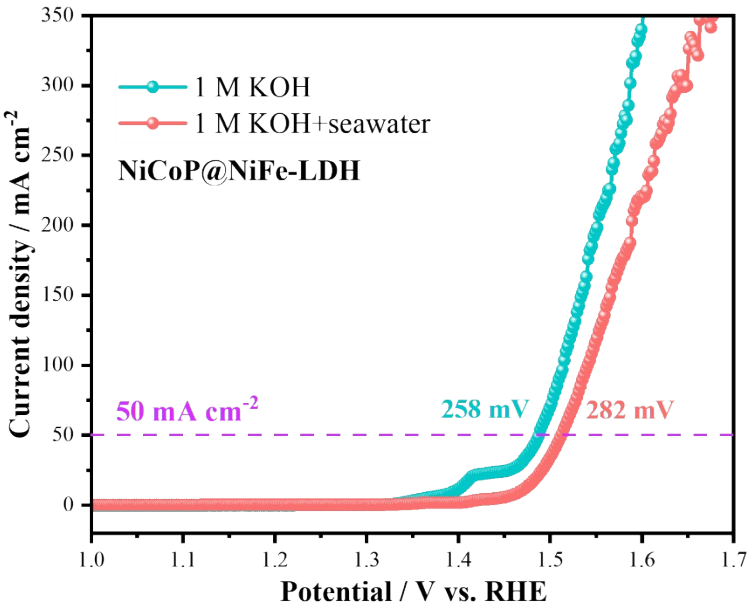

Fig. S3 OER Polarization curves of NiCoP@NiFe-LDH in different electrolytes.

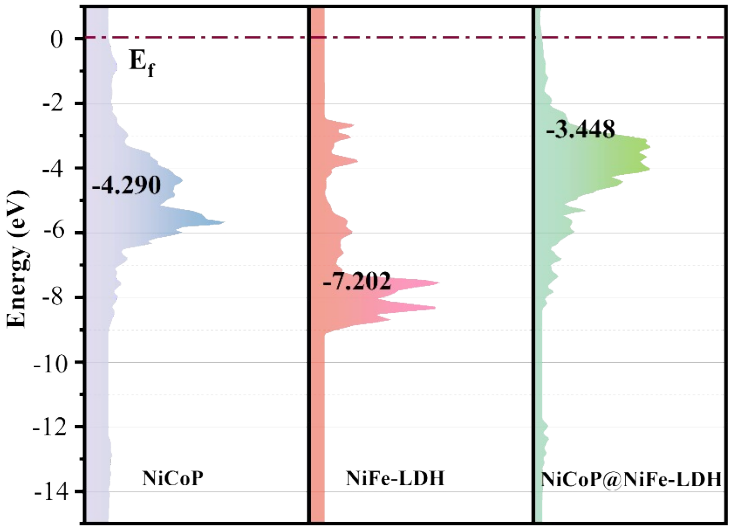

Fig. S4 The value of d band center of the three structures.

Table 1 Electrocatalytic performance of the samples

Catalysts	Overpotential	Tafel (mV dec^{-1})	Electrolyte	Ref.
NiFe-LDH/Ti_3C_2	OER:334 mV@10	55	1.0 M KOH	1
Ni-BDC@NiFe-LDH-2	OER:272 mV@10	45	1.0 M KOH	2
2.5Fe-NiCoP/PBA HNCs	OER:290 mV@10	70	1.0 M KOH	3
NiCoP-1.0	HER:84 mV@10	75.74	1.0 M KOH	4
CoFeP/CoP-400	HER:78 mV@10	55.5	1.0 M KOH	5
NiFe-LDH/MoS_2/CFP	HER:88.5mV@10	63.4	1.0 M KOH	6
NiFe-LDH/$FeCoS_2$/CFC	HER:308mV@10	157	1.0 M KOH	7
NiCoP@NiFe-LDH	HER:59mV@10	34.4	1.0 M KOH	This work
	OER:258mV@50	20.02		
	HER:100mV@10	41.07	1.0 M KOH + seawater	
	OER:285mV@50	25.19		

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