## **Supporting Information**

## Engineering the coupling interface of rhombic dodecahedral NiCoP/C@FeOOH nanocages toward advanced water oxidation

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**Fig. S1** XRD patterns of ZIF-67 (a), CoNi LDH/C and bare FeOOH (b), NiCoP/C and NiCoP/C@FeOOH (c).



**Fig. S2** SEM image of CoNi LDH/C and the corresponding EDS and elements analysis of the selected area.



**Fig. S3** SEM image of NiCoP/C and the corresponding EDS and elements analysis of the selected area.



Fig. S4 Line profiles of NiCoP/C collected from the HRTEM image.



Fig. S5 SEM image of NiCoP/C@FeOOH and the corresponding EDS and elements analysis of the selected area.



Fig. S6 SEM images of bare FeOOH with different magnifications.



Fig. S7 XPS spectra of NiCoP/C@FeOOH: (a) C 1s, (b) N 1s and (c) O 1s.

In Fig. S7(a), after carefully deconvolution and fitting, four peaks were split, namely 284.6 (C-C/C=C), 285.6 (C=N), 286.3 (C-O/C-N) and 289.2 (O-C=O) eV, confirming that the carbon framework was in-situ nitrogen-doped.<sup>5, 6</sup> More evidences were provided in Fig. S7(b)—N 1s core-level spectrum, in which four peaks were split, which were located at 397.6, 398.8, 401.1 and 402.1 eV, being associated to pyridinc-N, pyrrolic-N, graphitic-N and oxidized-N, respectively. This nitrogen signals unanimously validate the nitrogen doping of carbon framework.<sup>7</sup> Fig. S7(c) shows the XPS spectra of O 1s of the NiCoP/C@FeOOH, in which the peaks C=O (533.2 eV), Fe-O-H (532.2 eV) and Fe-O-Fe (531.2 eV) were deconvoluted.<sup>3, 4, 8</sup>



Fig. S8 XPS spectra of Fe 2p (a) and O 1s (b) of FeOOH.

The XPS spectra of Fe 2p are shown in Fig. S8(a). The peaks of Fe  $2p_{1/2}$  and Fe  $2p_{3/2}$  locating at 724.8 and 711.7 eV confirm that Fe element is mainly of Fe(III).<sup>1, 2</sup> The two satellite peaks at 733.59 and 719.39 eV further prove the +3 oxidation state of Fe.<sup>3, 4</sup> The XPS spectra of O 1s can be deconvoluted into two peaks at 529.8 and 531.6 eV (Fig. S8(b)), suggesting being associated to Fe-O-Fe and Fe-O-H units in this case, respectively, which are in agreement with FeOOH.<sup>3</sup>



Fig. S9 The Fe 2p XPS spectra comparison of FeOOH and NiCoP/C@FeOOH.



Fig. S10 CV curves of FeOOH, NiCoP/C and NiCoP/C@FeOOH.



Fig. S11 CV curves of (a) NiCoP/C@FeOOH, (b) NiCoP/C and (c) FeOOH with different scan rate.



**Fig. S12** SEM images of NiCoP/C@FeOOH with different magnifications which after 14 h stability test (a, b, c) and the corresponding EDS and elements analysis of the selected area (d).

Catalysts	Overpotential	Current	electrolyte	Ref.
(substrate)	(mV)	density		
		(mAm cm <sup>-2</sup> )		
NiCoP@FeOOH	271	10	1.0 M KOH	This work
Nanocages (GC)	321	50		
Nest-like NiCoP	290	10	1.0 M KOH	9
(CC)				,
NiCoP nanocone	370	10	1.0 M KOH	10
(NF)				10
NiCoP nanoparticles	320	10	1.0 M KOH	11
(ITO)				
NiCoP nanosheets	300	50	1.0 M KOH	12
Array (NF)				
FeOOH/Co/FeOOH	265	50	1.0 M NaOH	4
Nanotubes (NF)				·
Crystalized a-FeOOH	500	10	1.0 M KOH	13
(FTO)				15
CNTs@FeOOH	250	10	1.0 M KOH	14
Nanoflake (CC)				11
NiCo/NiCoOx	278	10	1.0 M KOH	15
with FeOOH (NF)				10
FeOOH/CeO <sub>2</sub>	250	20	1.0 M KOH	3
Nanotubes (NF)				5
Porous Ni-Fe selenide	255	35	1.0 M KOH	16
Nanosheets (CC)				10
NiCoP/C nanoboxes	330	10	1.0 M KOH	17
(CC)				17
$(Co_{0.54}Fe_{0.46})_2P$	370	10	0.1 M KOH	18
(CC)				10
Janus Ni <sub>0.1</sub> Co <sub>0.9</sub> P	570	5	1.0 M PBS	19
(CC)				17

**Table S1.** OER performance for some very recent reported 3d transition-metal based catalysts

Notes: Substrates NF: nickel foam; GC: glassy carbon electrode; CC: carbon cloth.

FTO: conducting glass (F: SnO<sub>2</sub>, FTO).

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