Supplementary Material

Ultralow Ru-assisted and Vanadium-doped Flower-like CoP/Ni_2P Heterostructure for Efficient Water Splitting in Alkali and Seawater

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Materials

Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H2O$), urea (CH_4N_2O), ammonium fluoride (NH_4F), sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) and potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ammonium metavanadate (NH_4VO_3) and Ruthenium chloride hydrate ($RuCl_3 \cdot xH_2O$) were purchased from Aladdin Chemical Reagent Co., Ltd. Acetone was purchased from Shanghai Chemical Reagent Company. RuO_2, Pt/C and Nafion (5 wt%) were purchased from Sigma-Aldrich. All reagents were used directly without purification.

Experimental section

Preparation of Ru-CoV-LDH/NF: 2*3 cm^2 nickel foam (NF) was sonicated successively in acetone and ethanol for 15 minutes to remove the surface oxide layer and impurities. 117 mg ammonium metavanadate, 1.164 g cobalt nitrate hexahydrate, 80 mg ammonium fluoride and 260 mg urea were stirred in 30 mL water at 50°C for 30min. Put the processed NF in the above solution and put it into a 50 mL reactor, and keep it at 120 °C for 360 min. After cooling to room temperature, CoV-LDH/NF was taken out and placed in $RuCl_3$ ethanol solution (20 mg/mL) for 1 h. Ru-CoV-LDH/NF can be obtained by vacuum drying at 60 ℃ for 12 hours. The loading mass of the catalyst is 3.6 mg cm^{-2}. Ru-Co-LDH/NF and CoV-LDH/NF were prepared without adding ammonium metavanadate and without immersing $RuCl_3$ solution as control samples.

Preparation of RuV-CoNiP/NF: 1.0g $NaH_2PO_2 \cdot H_2O$ was placed 10 cm upstream of the position of Ru-CoV-LDH/NF in the tube furnace. In argon, ventilate for 1 hour to drive out the air, and then increase the temperature to 350°C at a rate of 3°C per minute for 2 hours. Finally, the RuV-CoNiP/NF can be obtained by cooling to room temperature. Ru-CoNiP/NF and V-CoNiP/NF are prepared in the same way as RuV-CoNiP/NF.

Material Characterization

X-ray diffraction (XRD) was obtained on a Rigaku X-ray diffractometer equipped with a Cu Kα radiation source. The morphology and structure were characterized by scanning electron microscope (SEM, Zeiss Ultra Plus) and transmission electron microscope (TEM, HITACHIH-8100). X-ray photoelectron spectroscopy (XPS) was obtained on the type II X-ray photoelectron spectrometer. ICP-AES analysis obtained on Optima Prodigy 7 (LEEMAN LABS Ltd., USA).

Electrochemical Measurements

The electrochemical test is obtained in a three-electrode system with carbon rods and Hg/HgO as the counter electrode and reference electrode, and the electrolyte is 1 M KOH. The prepared catalyst is directly cut into a specific area to serve as a working electrode. The commercial electrocatalyst for comparison was obtained by first configuring RuO_2 and Pt/C as ink, and then evenly spreading it on the NF substrate (8 mg cm^{-2}). The workstation

used for the test is CHI 660E electrochemical analyzer (CHI Instruments, Shanghai, China). The polarization curves of OER and HER have been iR corrected ($E_{iR\text{-}corrected} = E - iR$, where E is the original potential, R is the solution resistance, i is the corresponding current, and $E_{iR\text{-}corrected}$ is the iR-corrected potential). The voltages of HER and OER are both converted to the RHE scale by the formula E (vs. RHE) = E (vs. Hg/HgO) + 0.059*pH + 0.098 V. The frequency range of the electrochemical impedance spectroscopy (EIS) test is 0.01 Hz to 100 kHz, and the AC amplitude is 10 mV. To obtain the electrochemical double layer capacitance (C_{dl}), cyclic voltammetry (CV) was performed at different scan rates (20, 40, 60, 80 and 100 mV s^{-1}) of 0 ~ 0.1 V vs Hg/HgO.

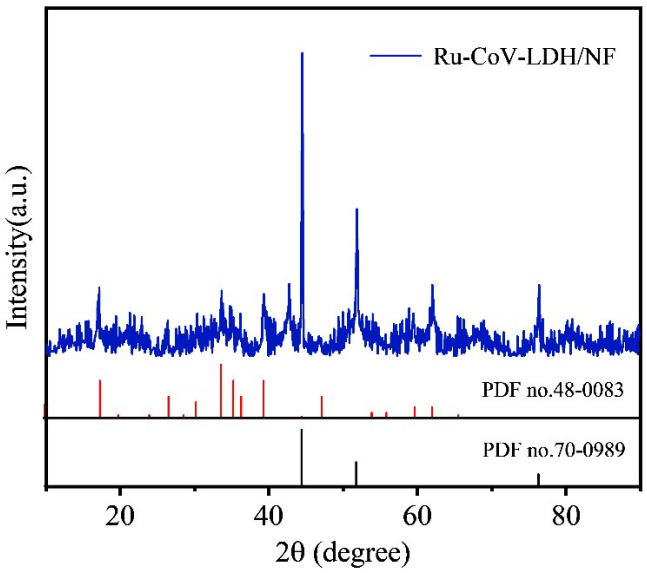

Figure S1. XRD pattern of Ru-CoV-LDH/NF.

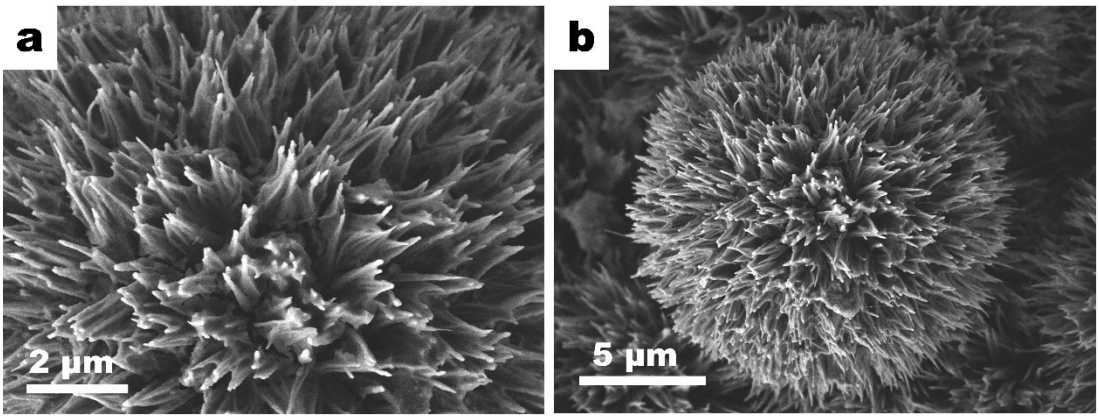

Figure S2. SEM images of Ru-CoV-LDH/NF.

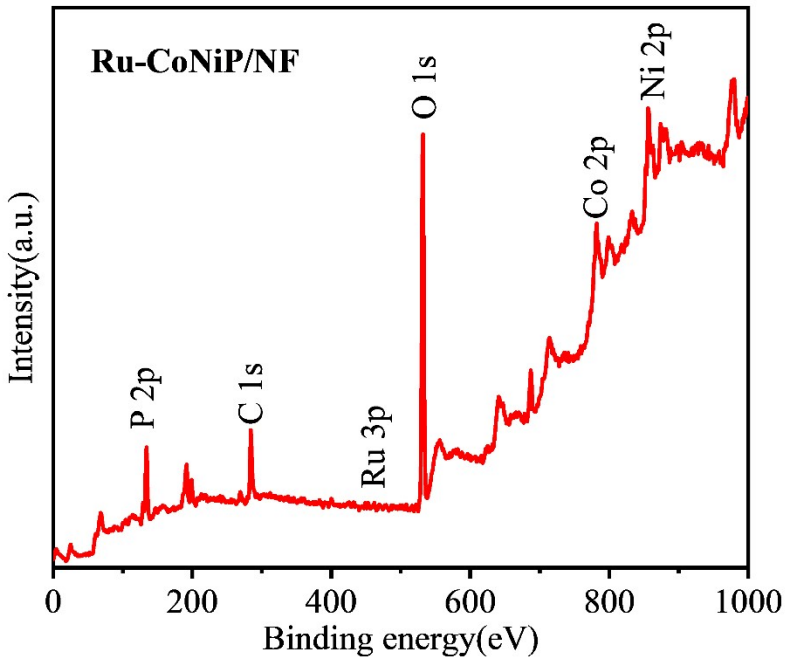

Figure S3. XPS survey pattern of Ru-CoNiP/NF.

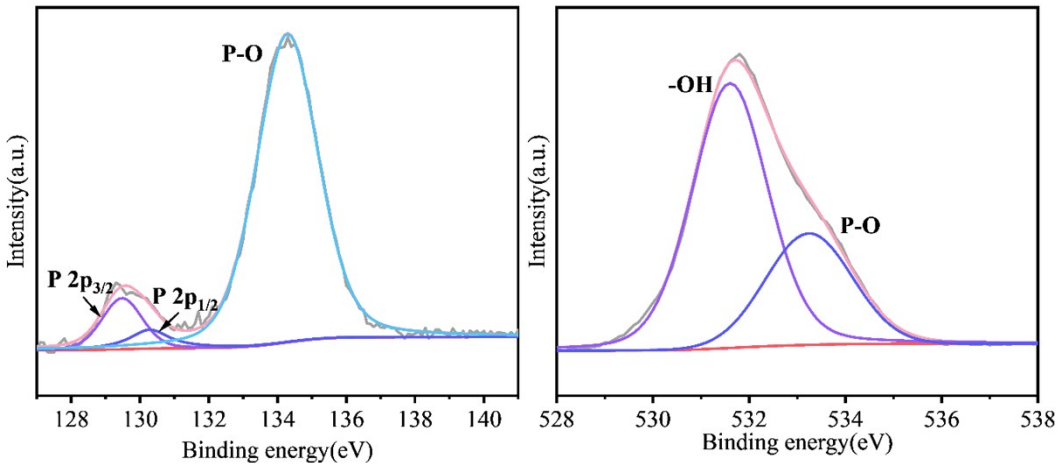

Figure S4. O 1s and P 2p of RuV-CoNiP/NF spectra.

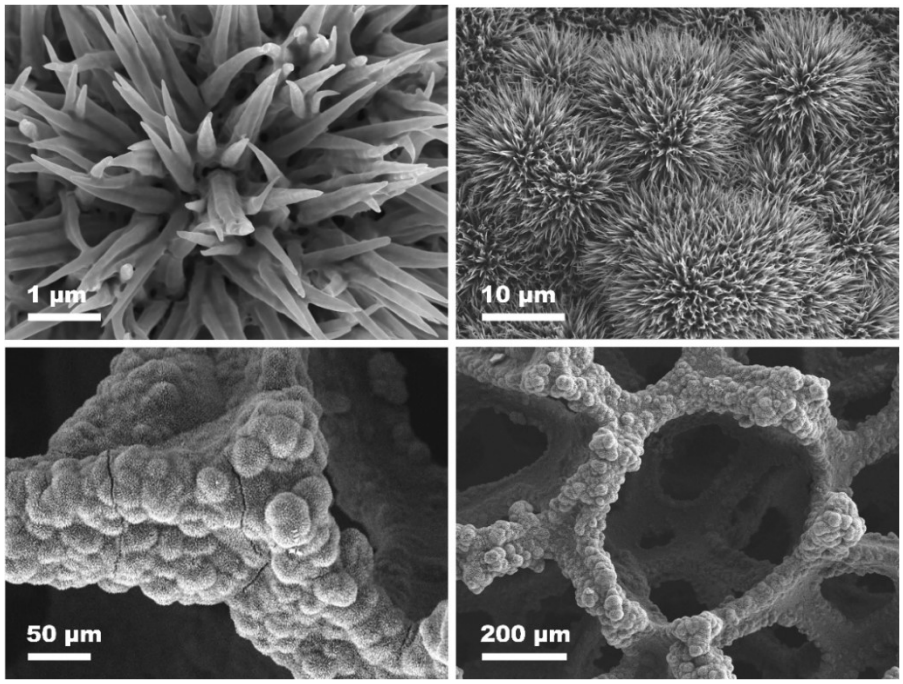

Figure S5. SEM images of RuV-CoNiP/NF.

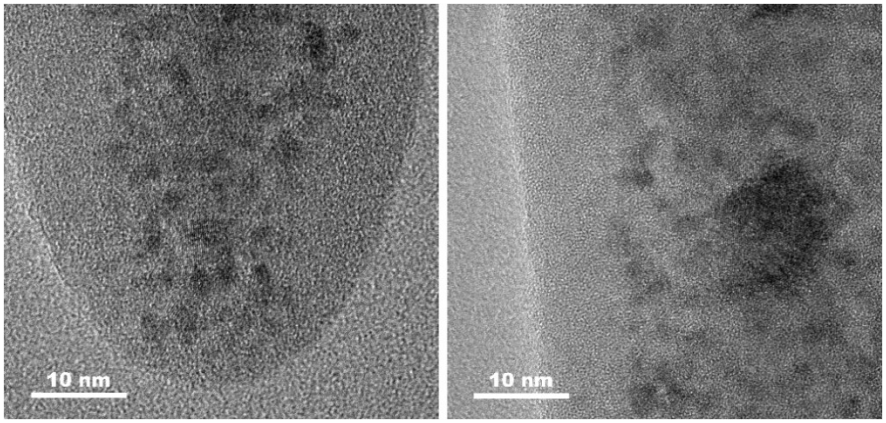

Figure S6. TEM images of RuV-CoNiP/NF.

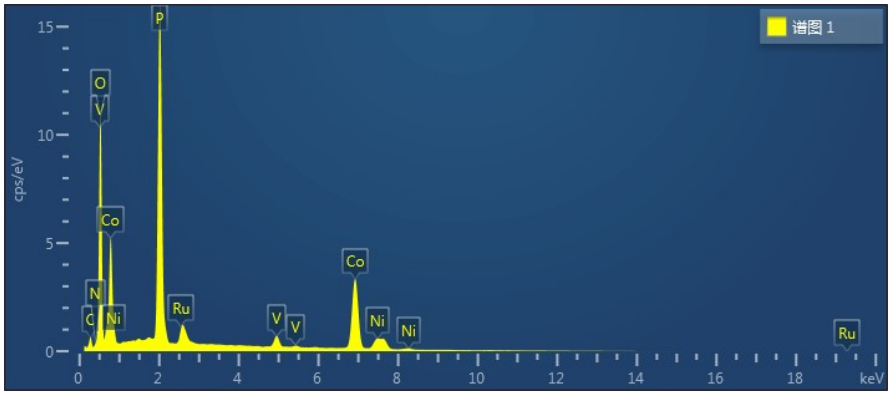

Figure S7. EDX spectrum of RuV-CoNiP/NF.

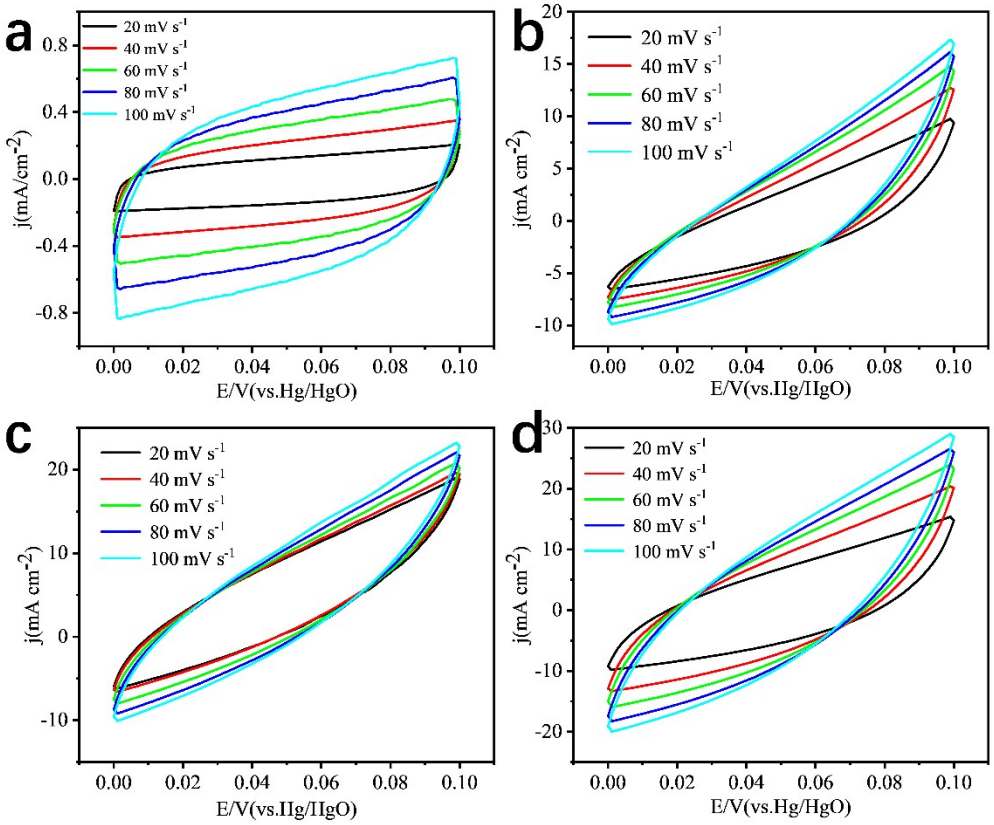

Figure S8. Cyclic voltammograms of (a) bare NF, (b) V-CoNiP/NF, (c) Ru-CoNiP/NF and (d) RuV-CoNiP/NF in the non-faradic capacitance current range from 20 to 100 mV s^{-1}.

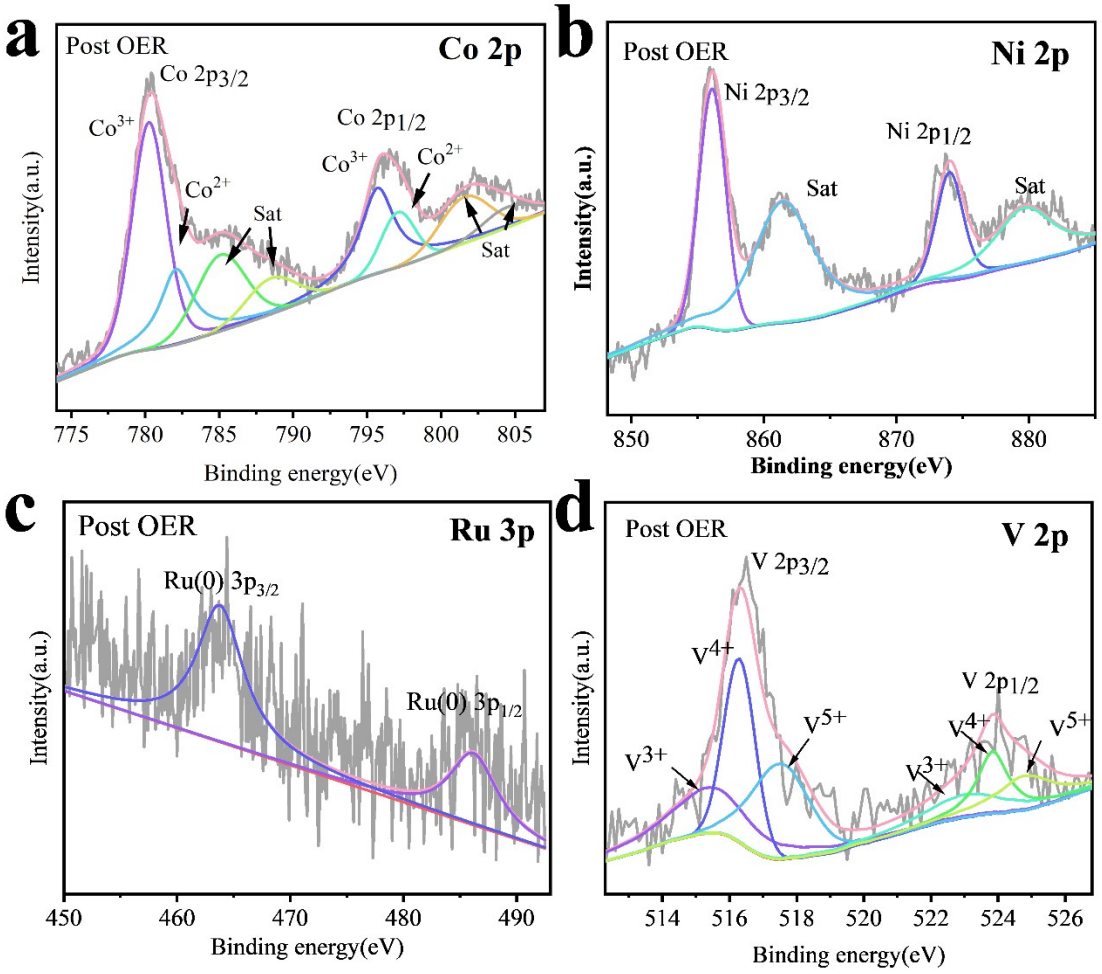

Figure S9. (a) Co 2p, (b) Ni 2p, (c) Ru 3p and (d) V 2p of RuV-CoNiP/NF spectrums after OER test.

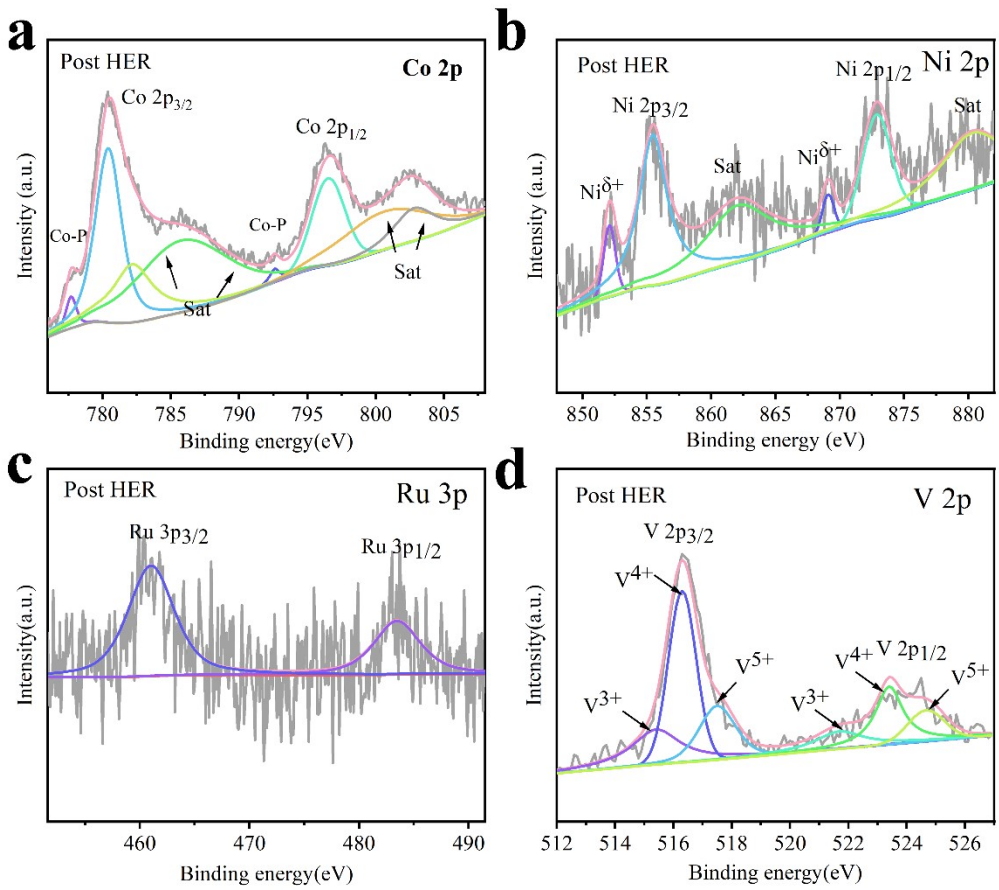

Figure S10. (a) Co 2p, (b) Ni 2p, (c) Ru 3p and (d) V 2p of RuV-CoNiP/NF spectrums after HER test.

Figure S11. (a-b) Changes in the volume of (a) O_2 and (b) H_2 over time.

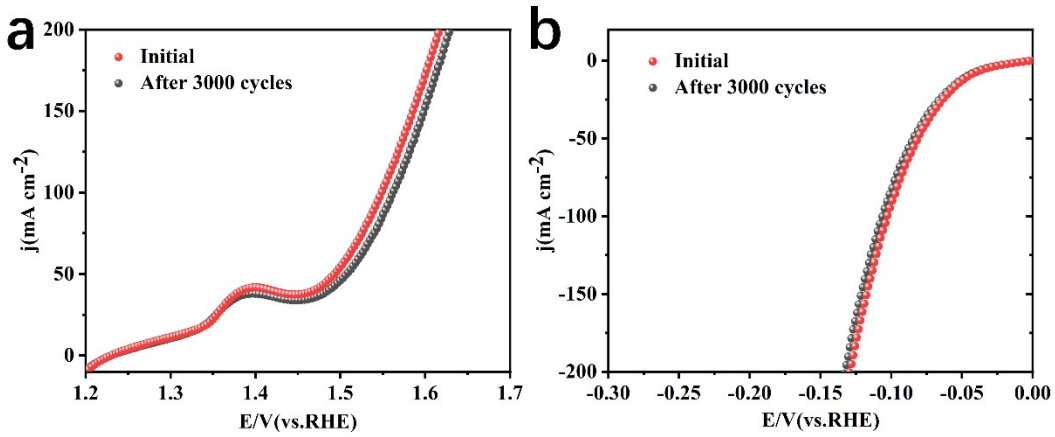

Figure S12. LSV curves of RuV-CoNiP/NF before and after accelerated durability test in alkaline seawater

Table S1. Ni, Co, Ru, V, P, N, C and O atomic percentages of RuV-CoNiP/NF in XPS survey scan.

Sample	Ni	Co	Ru	V	P	N	C	O
atomic percentages	11.56	5.47	0.47	0.76	9.96	1.73	27.07	42.98

Table S2. Ni, Co, Ru, V, P, N, C and O atomic percentages of RuV-CoNiP/NF in EDS elemental mapping.

Sample	Ni	Co	Ru	V	P	N	C	O
atomic percentages	3.23	20.11	0.69	1.45	21.06	1.54	10.54	41.38

Table S3. Ni, Co, Ru, V and P weight percentages of RuV-CoNiP/NF in inductively coupled plasma (ICP).

Sample	Ni	Co	Ru	V	P
Weight percentages	23.85	41.66	4.65	10.00	19.84

Table S4. Performance comparison of RuV-CoNiP/NF and recently reported self-supporting OER catalysts in 1M KOH.

Catalyst	Support	Overpotential@j (mV @ mA cm^{-2})	Mass loading (mg cm^{-2})	reference
RuV-CoNiP	Nickel foam	214@20 245@50 266@100	3.6	This work
IrNi-$FeNi_3$	Nickel foam	240@20	not provided	1
Co_4N-CeO_2/GP	Graphitic Plate	239@10	4.0	2
(Ru–Co)O_x	Carbon cloth	171@10	not provided	3
$Fe_xNi_{3-x}S_2$	Nickel foam	252@100	not provided	4
$Ni^{III}Co^{II}Fe$-O	Nickel foam	258@50	not provided	5
NF-Na-Fe-Pt	Nickel foam	261@10	not provided	6
CoFeZr oxides	Nickel foam	264@20	not provided	7
Co-Co_2C	Carbon cloth	261@10	3.2	8
Ni-Mo_2C/NC	Nickel foam	337@10	2.5	9
Fe-CoP	Nickel foam	190@10	4.2	10
Ru-NiCoP	Nickel foam	216@20	not provided	11
Ru–MnFeP	Nickel foam	191@20	not provided	12
$MoNi_3S_2/Ni_xP_y$	Nickel foam	238@50	3.15	13

CoFe PBA@CoP	Nickel foam	171@10	not provided	14
V-doped CoP	Nickel foam	265@20	not provided	15
CoMnP/Ni_2P	Nickel foam	209@10	1.62	16
Ni_2P-Fe_2P	Nickel foam	261@10	15	17
Co_2P-Ni_2P	Nickel foam	230@50	1.51	18

Table S5. Performance comparison of RuV-CoNiP/NF and recently reported self-supporting HER catalysts in 1M KOH.

Catalyst	**Support**	**Overpotential@j (mV @ mA cm^{-2})**	**Mass loading (mg cm^{-2})**	**reference**
RuV-CoNiP	Nickel foam	28@10	3.6	This work
IrNi-$FeNi_3$	Nickel foam	31.1@10	not provided	1
Co_4N-CeO_2/GP	Graphitic Plate	24@10	4.0	2
(Ru–Co)O_x	Carbon cloth	44.1@10	not provided	3
$Fe_xNi_{3-x}S_2$	Nickel foam	72@10	not provided	4
$Ni^{III}Co^{II}Fe$-O	Nickel foam	58@10	not provided	5
NF-Na-Fe-Pt	Nickel foam	31@10	not provided	6
CoFeZr oxides	Nickel foam	104@10	not provided	7

Co-Co_2C	Carbon cloth	96@10	3.2	8
Ni-Mo_2C/NC	Nickel foam	40@10	2.5	9
Fe-CoP	Nickel foam	78@10	4.2	10
Ru-NiCoP	Nickel foam	44@10	not provided	11
Ru–MnFeP	Nickel foam	35@10	not provided	12
$MoNi_3S_2/Ni_xP_y$	Nickel foam	109@10	3.15	13
CoFe PBA@CoP	Nickel foam	100@10	not provided	14
V-doped CoP	Nickel foam	84.6@10	not provided	15
CoMnP/Ni_2P	Nickel foam	108@10	1.62	16
Ni_2P-Fe_2P	Nickel foam	128@10	15	17
Co_2P-Ni_2P	Nickel foam	90@10	1.51	18

Table S6. Performance comparison of RuV-CoNiP/NF and recently reported self-supporting water splitting catalysts in 1M KOH.

Catalyst	**Support**	**Cell voltage@j (V@mA cm^{-2})**	**Mass loading (mg cm^{-2})**	**reference**
RuV-CoNiP	Nickel foam	1.469 V@10	3.6	This work
IrNi-$FeNi_3$	Nickel foam	1.47@10	not provided	1
Co_4N-CeO_2	Graphitic Plate	1.507@10	4.0	2

$(Ru–Co)O_x$	Carbon cloth	1.488@10	not provided	3
$Fe_xNi_{3-x}S_2$	Nickel foam	1.51@10	not provided	4
$Ni^{III}Co^{II}Fe$-O	Nickel foam	1.455@10	not provided	5
NF-Na-Fe-Pt	Nickel foam	1.56@10	not provided	6
CoFeZr oxides	Nickel foam	1.63@20	not provided	7
Co-Co_2C	Carbon cloth	1.63@10	3.2	8
Ni-Mo_2C/NC	Nickel foam	1.59@10	2.5	9
Fe-CoP	Nickel foam	1.49@10	4.2	10
Ru-NiCoP	Nickel foam	1.515@10	not provided	11
Ru–MnFeP	Nickel foam	1.47@10	not provided	12
Mo-Ni_3S_2/Ni_xP_y	Nickel foam	1.46@10	3.15	13
CoFe PBA@CoP	Nickel foam	1.542@10	not provided	14
V-doped CoP	Nickel foam	1.53@10	not provided	15
CoMnP/Ni_2P	Nickel foam	1.54@10	1.62	16
Ni_2P-Fe_2P	Nickel foam	1.561@10	15	17
Co_2P-Ni_2P	Nickel foam	1.47@10	1.51	18

Notes and References

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