Electronic Supplementary Information for

Boosting hydrogen evolution activity of vanadyl pyrophosphate nanosheets for electrocatalytic overall water splitting

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Experimental Section

Synthesis of $(VO)_2P_2O_7$ samples

The 2D $(VO)_2P_2O_7$ nanosheets were fabricated via the hydrothermal process and heat treatment. The details are as follows: 1.0 g V_2O_5 and 12 ml H_3PO_4 were dissolved in 24 mL deionized water and stirred about 30 minutes to form a clear solution. Then, the aqueous reagent solution was put into a 50 mL Teflon-lined stainless-steel autoclave, which was sealed and maintained at 104 ºC for 20 h. After that, the deposit was filtered, washed with deionized water and alcohol, and dried at 80 ºC for 24 h. Finally, 2D $(VO)_2P_2O_7$ nanosheets were obtained by heated at 250 ºC for 12 h in an Ar atmosphere.
The bulk $(VO)_2P_2O_7$ was also synthesized by the followed method. 1.0 g V_2O_5 with 5.2 ml H_3PO_4 was dissolved in 24 ml distilled water and stirred under reflux at 120 °C for 8 h. The yellow solid was recovered by vacuum filtration, washed with distilled water and acetone and then dried in the air at 110 °C for 16 h. After refluxed for 20 h in 80 ml of isobutanol, the obtained materials were filtered out from the solvent, washed with acetone, and dried for 16 h at 110 °C. Finally, the precursors were heated at 550 °C for 4 h under N_2 flow conditions in a tube furnace to get the bulk $(VO)_2P_2O_7$.

Characterizations

XRD patterns were performed by an X-ray diffractometer (SmartLab 9kW) at a scan rate of 1° min^{-1} from 5 to 70°. The N_2-sorption isotherms and pore size distribution curves for the $(VO)_2P_2O_7$ nanosheets were obtained by the Brunauer–Emmett–Teller (BET) measurement with an Autosorb-iQ-MP Micromeritics analyzer. The field-emission-gun SEM instruments (Quanta FEG 250 and Verios 460L of FEI) were applied in the SEM characterization. TEM and EDS images were achieved via TEM instruments, namely JEOL JEM-2100 and FEI Talos F200X. XPS results were recorded by a Kratos AXIS Ultra DLD system with the Al Kα radiation as the X-ray source. Meanwhile, the C 1s peak has been fixed at the binding energy of 284.8 eV.

Electrochemical measurements

All electrochemical tests were executed on a CHI electrochemical instrument (760E) under the 1.0 M KOH solution and room temperature (25 °C). HER and OER performances were carried out in a three-electrode system, and the OWS performance was tested in a two-electrode full cell. In the three-electrode system, Hg/HgO electrode, graphite rod, and rotating disk electrode loaded with the catalyst were used as the reference electrode, counter electrode, and working electrode, respectively. As for HER and OER experiments, linear sweep voltammetry (LSV) was tested with sweep rates of 5 mV s^{-1} at a rotation rate of 1600 rpm in the N_2-saturated and O_2-saturated solution, respectively. In the full cell system, two $(VO)_2P_2O_7$ electrodes served as both of the anode and cathode at the same time. IrO_2 and Pt/C electrodes were applied as the benchmark sample. *i*R compensation was applied to all initial data except stability data. All of the HER and OER potential values were calculated according to the equation, $E_{RHE} = E_{Hg/HgO} + 0.098\ V + 0.059\ pH$.

To prepare the working electrode, 3.5 mg of the sample was dispersed in a solution, including 500 μL 0.5 wt.% Nafion and 500 μL deionized water. As for glassy carbon electrode (0.196 cm^{-2} for active geometric area), 39 μL solution applied in HER and 84 μL solution applied in OER were dropped at electrodes and dried in room temperature. The catalyst loadings on electrodes for HER and OER tests were 0.7 mg cm^{-2} and 1.5 mg cm^{-2}, respectively. As a comparison, the Pt/C and IrO_2 (20 wt.%) electrodes hold the same loading.

TOF values were calculated by the following equation:

$$\mathrm{TOF} = j\mathrm{A}/(2\mathrm{F}n)$$

where j is the current density at a given overpotential (η), A is the surface area of the working electrode (0.196 cm^{-2}), F is the Faraday constant and n is the mole of active sites on the working electrode. The Tafel plots were derived from the polarization curves. The ECSA values of the samples were believed to be linearly proportional to electrochemical double-layer capacitance (C_{dl}) values. The C_{dl} values were determined by cyclic voltammetry (CV) curves measured in non-Faradaic regions at scan rates of 5, 10, 15, 20 and 25 mV s^{-1}. The EIS measurements were performed in 1.0 M KOH at an open-circuit potential state in a frequency range from 0.01 Hz to 100 KHz with an alternating current (AC) voltage amplitude of 5 mV.

Computational details

The details of our DFT calculations are given in our previous work (*J. Catal.* 2018, 364, 125).

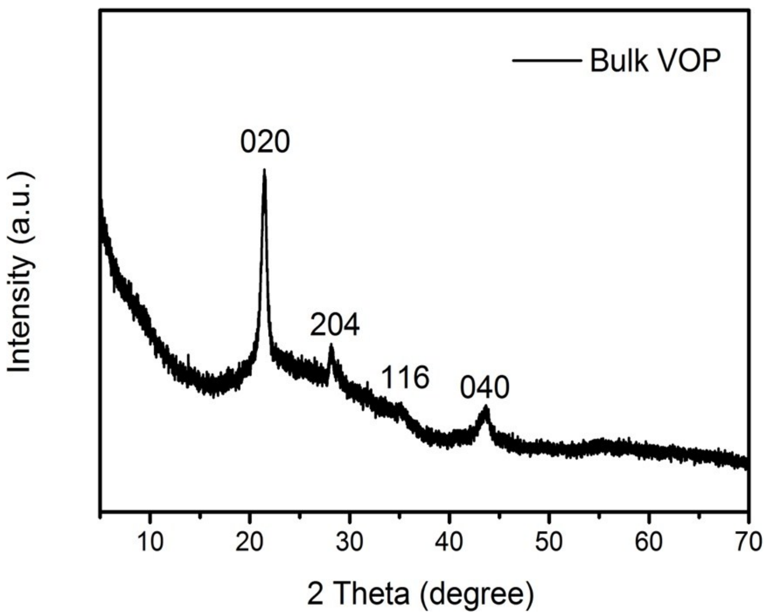


Figure S1. The XRD pattern of bulk VOP.

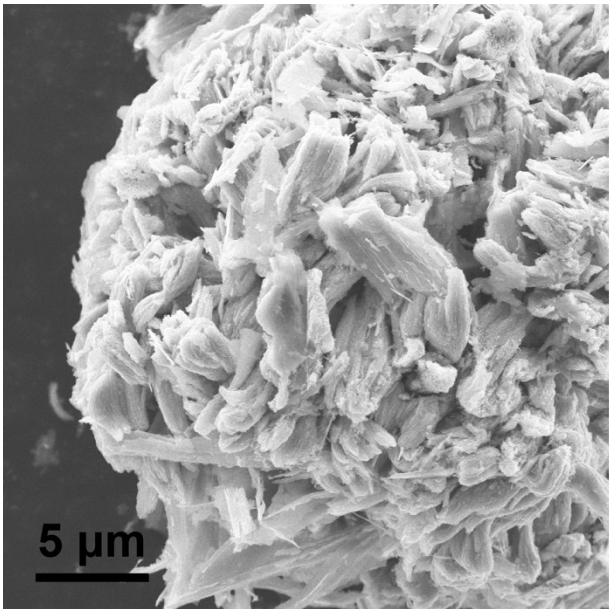


Figure S2. The SEM image of bulk VOP.

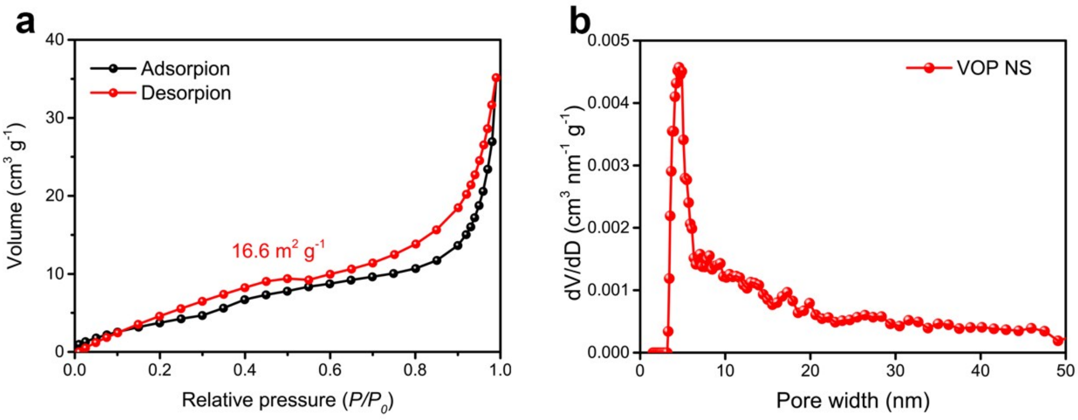


Figure S3. The N_2 adsorption–desorption isotherm (a) and the corresponding pore size distribution (b) for VOP NS.

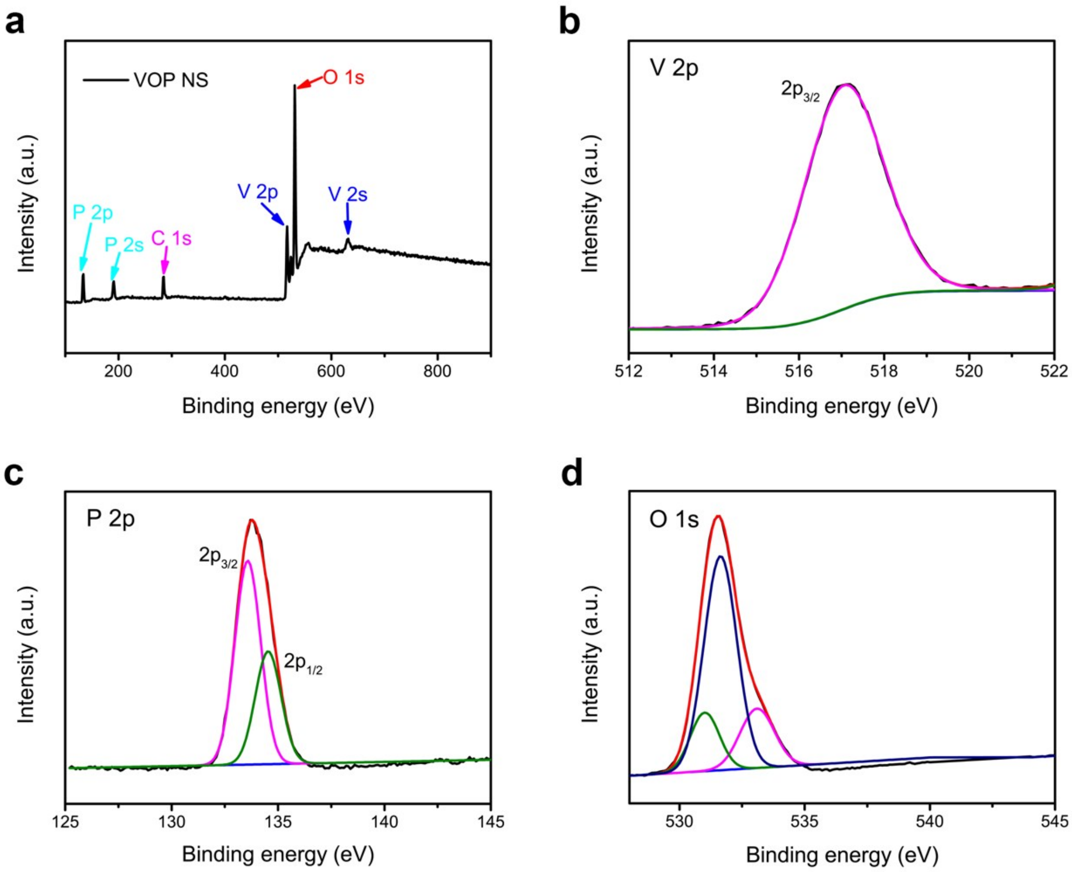
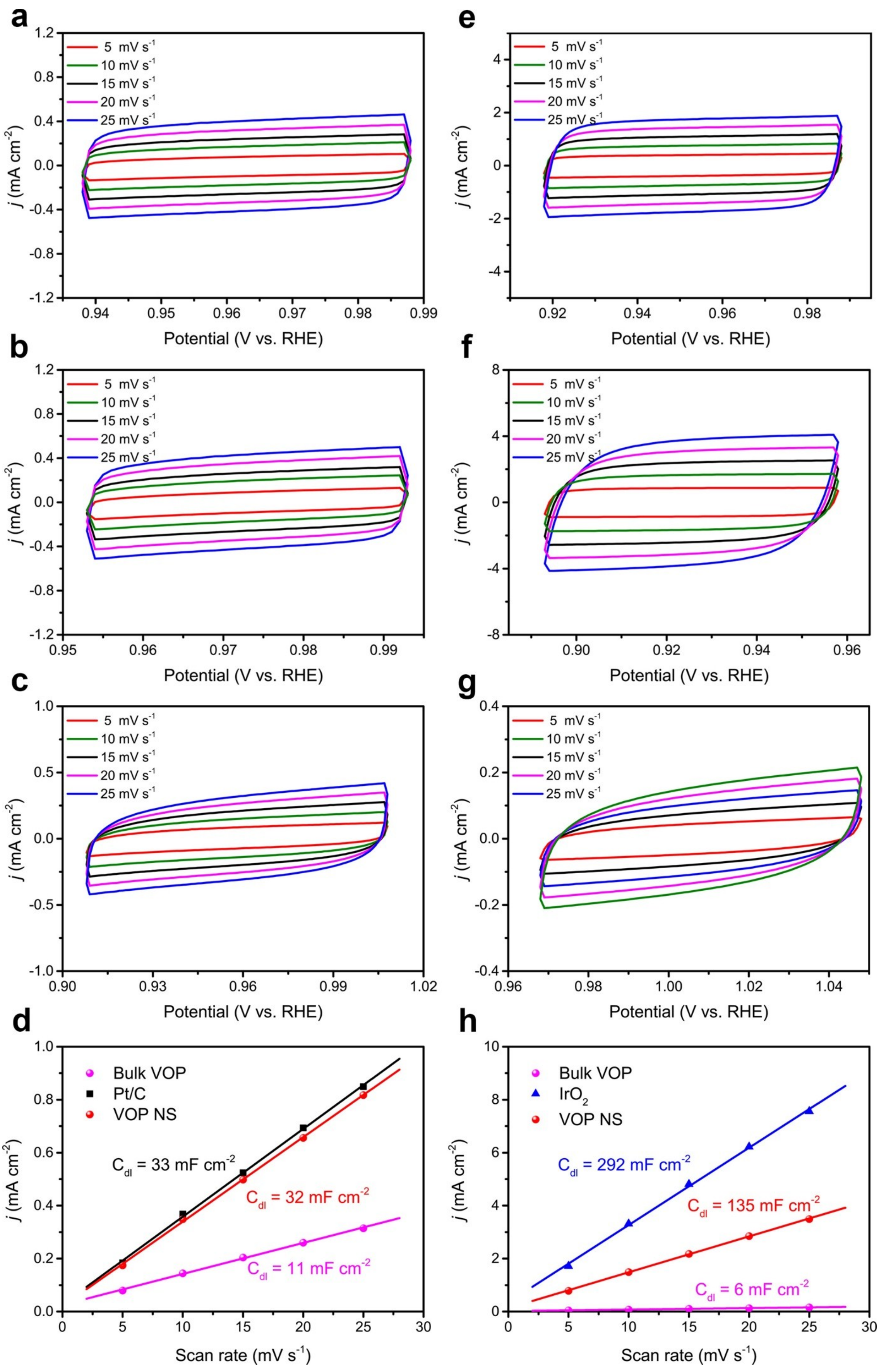


Figure S4. XPS spectra for VOP NS. (a) XPS survey spectrum. (b) V 2p. (c) P 2p. (d) O 1s.



a
b
c
d
e
f
g
h
5 mV s-1
10 mV s-1
15 mV s-1
20 mV s-1
25 mV s-1
j (mA cm-2)
Potential (V vs. RHE)
Bulk VOP
Pt/C
VOP NS
IrO2
Cdl = 33 mF cm-2
Cdl = 32 mF cm-2
Cdl = 11 mF cm-2
Cdl = 292 mF cm-2
Cdl = 135 mF cm-2
Cdl = 6 mF cm-2
Scan rate (mV s-1)

Figure S5. (a–c) CVs of VOP NS, Pt/C and bulk VOP measured in non-Faradaic regions at scan rates of 5, 10, 15, 20 and 25 mV s^{-1} under HER condition and (d) corresponding C_{dl} values, respectively. (e–h) have the same meanings as (a–d) but under OER condition.

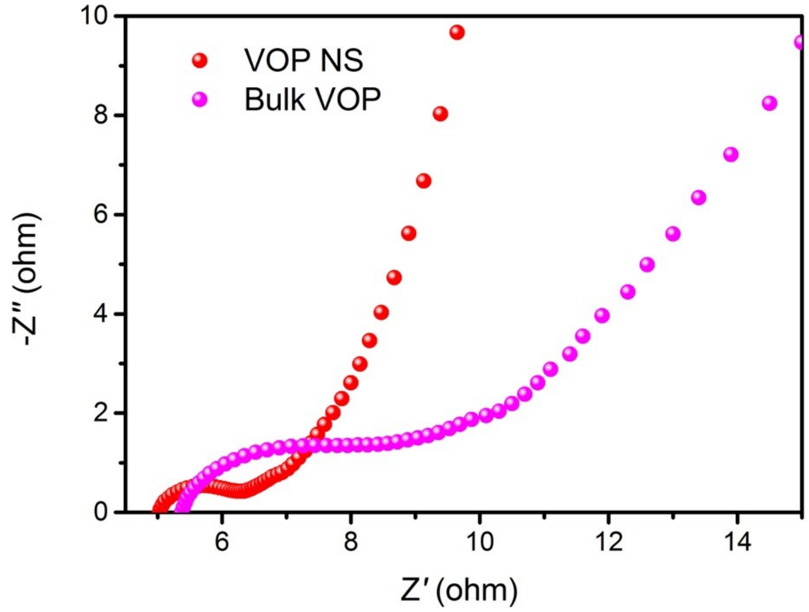


Figure S6. The EIS results of VOP NS and bulk VOP.

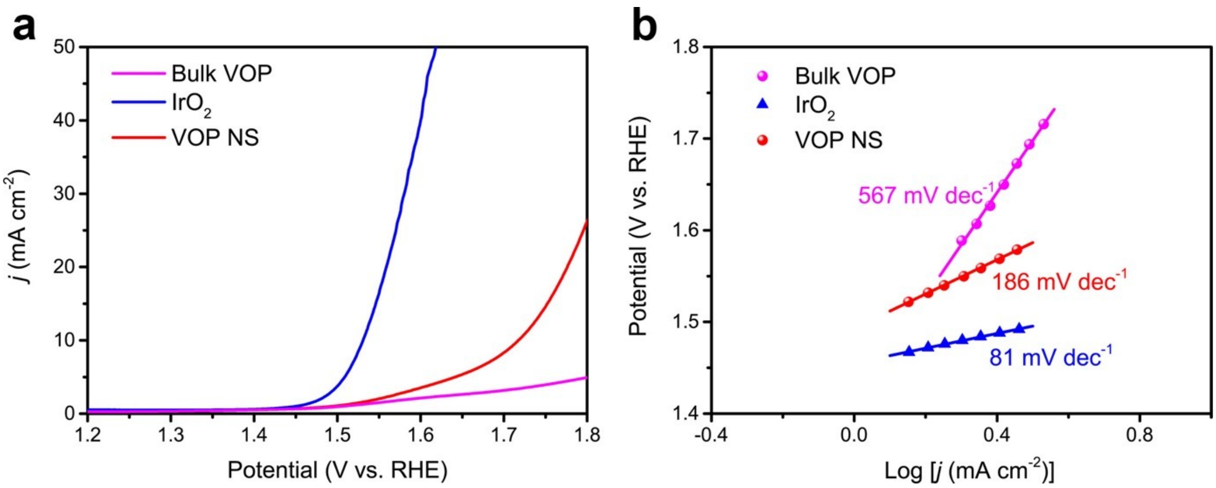


Figure S7. (a) OER polarization curves and (b) corresponding Tafel plots for VOP NS, IrO_2 and bulk VOP.

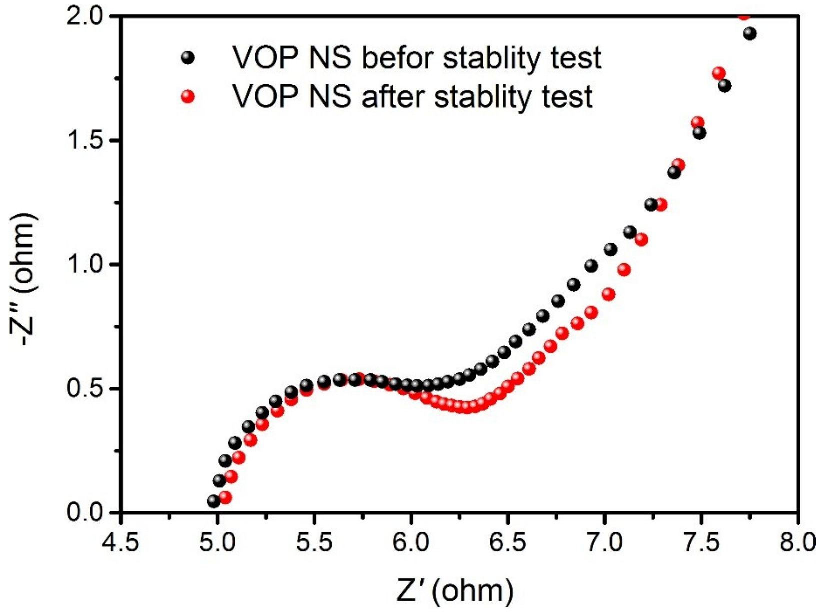


Figure S8. The EIS results of VOP NS before and after the chronoamperometric test. The red curve of VOP NS in Figure S6 is redrawn here as the black one.

Table S1. HER electrocatalysis results of this work and those reported in the literature.

Electrocatalyst	Electrolyte	η [mV] for j_{HER} = 10 mA cm^{-2}	Tafel [mV dec^{-1}]	Stability	Reference
δ-WN/Co	1 M KOH	76	98	36,000 s (97% of –10 mA cm^{-2} at –0.076 V)	*J. Mater. Chem. A*, **2018**, *6*, 10967
$Zn_{1-x}Fe_x$-LDH/Ni-foam	1 M KOH	221	150	10,800 s (100% ~ –0.4 V of at –50 mA cm^{-2})	*Small.* **2018**, *14*, 1803638
W-SAC	0.1 M KOH	85	53	10,000 cycles (100%)	*Adv. Mater.* **2018**, *30*, 1800396
$Ru_{0.33}Se$ @ TNA	1 M KOH	57	50	36,000 s (100% ~ –10 mA cm^{-2} of at –0.1 V)	*Small* **2018**, *14*, 1802132
V_8C_7@GC NSs/NF	1 M KOH	47	44.5	360,000 s (100% ~ –0.051 V of at –10 mA cm^{-2})	*Adv. Energy Mater.* **2018**, *8*, 1800575
S-MoS_2@C	1 M KOH	155	99	86,400 s (100% ~ –0.2 V of at –10 mA cm^{-2})	*Adv. Energy Mater.* **2019**, *9*, 1802553
Ni_4Mo nanosheets	1 M KOH	35	45	1,000 cycles	*small* **2017**, *13*, 1701648
MPM-2	1 M KOH	78	43	3,000 cycles (100%)	*Angew. Chem.* **2018**, *130*, 14335
Pt@PCM	1 M KOH	139	73.6	18,000 s (>95% of ~ –11 mA cm^{-2} at –0.15 V)	*Sci. Adv.* **2018**, *4*, 6657
Ni_3Fe@N-C NT/NFs	1 M KOH	72	98	40,000 s (100% of ~ –20 mA at –0.2 V)	*Adv. Funct. Mater.* **2018**, *28*, 1805828
porous Ni_2P NS	1 M KOH	168	63	36,000 s (100% of –10 mA cm^{-2} at –0.4 V vs SCE)	*J. Mater. Chem. A*, **2018**, *6*, 18720
Rh/SWNTs	1 M KOH	48	27	10,000 cycles (100%)	*ACS Catal.* **2018**, *8*, 8092
$MoNi_4/MoO_{3-x}$	1 M KOH	17	23	72,000 s	*Adv. Mater.* **2017**, *29*, 1703311

NFP/C-3	1 M KOH	95	72	43,200 s (100% of ~ –0.1 V at –10 mA cm^{-2})	*Sci. Adv.* **2019**, *5,* 6009
Ni_3N/Ni/NF	1 M KOH	12	29.3	180,000 s (100% of ~ –0.02 V at –10 mA cm^{-2})	*Nat. Commun.* **2018**, *9,* 4531
S-MoP NPL	1 M KOH	104	56	30,000 s (100% of ~ –0.12 V at –10 mA cm^{-2})	*ACS Catal.* **2019**, *9,* 651
CoP/Co-MOF	1 M KOH	34	56	30,000 s (100% of ~ –0.07 V at –20 mA cm^{-2})	*Angew. Chem.* **2019**, *131*, 4727
EBP@NG	1 M KOH	190	76	57,600 s (~ 90% at –20 mA cm^{-2})	*J. Am. Chem. Soc.* **2019**, *141*, 4972
N-Co_2P/CC	1 M KOH	34	51	120000 s (100% of ~ –0.05 V at –10 mA cm^{-2})	*ACS Catal.* **2019**, *9,* 3744
Ni NP|Ni-N-C	1 M KOH	147	114	36,000 s (100% of ~ –30 mA cm^{-2} at –0.3 V)	*Energy Environ. Sci.*, **2019**, *12*, 149
Ni, Zn dual-doped CoO NRs	1 M KOH	53	47	36,000 s (100% of ~ –10 mA cm^{-2} at –0.53 V)	*Adv. Mater.* **2019**, *31,* 1807771
VOP NS	1 M KOH	30	40	72,000 s & 1,000 cycles (100%)	***This work***

Table S2. OWS electrocatalysis results of this work and those reported in the literature.

Electrocatalyst	Electrolyte	OWS operating voltage [V]	Stability	Reference
$(Ni_{0.33}Fe_{0.67})_2P$	1 M KOH	1.49	39,600 s (96.6% of 100 mA cm^{-2} at 1.7 V)	*Adv. Funct. Mater.* **2017***, 27,* 1702513
Cu@NiFe LDH	1 M KOH	1.54	172,800 s (100% of ~ 1.54 V at 10 mA cm^{-2})	*Energy Environ. Sci.,* **2017***,10,* 1820
FeP/Ni2P	1 M KOH	1.57	144,000 s (100% of ~ 1.7 V at 500 mA cm^{-2})	*Nat. Commun.* **2018**, 9, 2551
NC-NiCu-NiCuN	1 M KOH	1.56	180,000 s (100% of ~ 9 mA cm^{-2} at 1.52 V)	*Adv. Funct. Mater.* **2018***, 28,* 1803278
Pt-CoS_2/CC	1 M KOH	1.55	72,000 s (100% of ~ 1.55 V at 10 mA cm^{-2})	*Adv. Energy Mater.* **2018***, 8,* 1800935
$Ni_{0.75}Fe_{0.125}V_{0.125}$-LDHs	1 M KOH	1.59	54,000 s (100% of ~ 1.7 V at 30 mA cm^{-2})	*Small* **2018***, 14,* 1703257
FeB_2-NF	1 M KOH	1.57	86,400 s	*Adv. Energy Mater.* **2017***, 7*, 1700513
Se-(NiCo)S/OH	1 M KOH	1.60	237,600 s (100% of ~ 10 mA cm^{-2} at 1.6 V)	*Adv. Mater.* **2018***, 30,* 1705538
CoP-Co2P@PC/PG	1 M KOH	1.57	108,400 s (100% of ~ 10 mA cm^{-2} at 1.567 V)	*Small* **2019***, 15,* 1804546
Co_1Mn_1CH	1 M KOH	1.68	50,400 s (100% of ~ 1.68 V at 10 mA cm^{-2})	*J. Am. Chem. Soc.* **2017***, 139,* 8320
Co_3Se_4/CF	1 M KOH	1.59	3581 h (100% of ~ 1.6V at 10 mA cm^{-2})	*Adv. Energy Mater.* **2017***, 7*, 1602579
EBP@NG	1 M KOH	1.54	21,600 s (> 97% of 1.54 V at 10 mA cm^{-2})	*J. Am. Chem. Soc.* **2019***, 141,* 4972
$CoSn_2$/NF	1 M KOH	1.55	57,600 s (100% of 10 mA cm^{-2} at 1.55 V)	*Angew. Chem.* **2018***, 130,* 15457

NiFe NTAs-NF	1 M KOH	1.62	72,000 s (100% of ~ 1.62 V at 10 mA cm^{-2})	*ACS Appl. Energy Mater.* **2018**, *1,* 1210
PdP_2@CB	1 M KOH	1.72(50 mA cm^{-2})	36,000 s (100% of ~ 50 mA cm^{-2} at 1.72 V)	*Angew. Chem.* **2018**, *130,* 15078
$Co_{0.75}Ni_{0.25}(OH)_2$	1 M KOH	1.56	54,000 s (100% of ~ 1.57 V at 10 mA cm^{-2})	*Small* **2019**, *15,* 1804832
C/CuCo/$CuCoO_x$	1 M KOH	1.53	360,000 s (100% of ~ 49 mA cm^{-2} at 1.65 V)	*Adv. Funct. Mater.* **2018**, *28,* 1704447
$Ni_{0.8}Co_{0.1}Fe_{0.1}O_xH_y$	1 M KOH	1.58	180,000 s (100% of ~ 1.58 V at 10 mA cm^{-2})	*ACS Catal.* **2018**, *8,* 5621
CoP/NCNHP	1 M KOH	1.64	129,600 s	*J. Am. Chem. Soc.* **2018**, *140,* 2610
NiCoP/CC	1 M KOH	1.52	40,000 s (~ 95% of ~ 1.78 V at 100 mA cm^{-2})	*ACS Catal.* **2017**, *7,* 4131
Cr-doped FeNi-P/NCN	1 M KOH	1.50	72,000 s (~ 98% of 1.50 V at 10 mA cm^{-2})	*Adv. Mater.* **2019**, *31,* 1900178
O-CoMoS	1 M KOH	1.60	36,000 s (100% of ~ 10 mA cm^{-2} at 1.6 V))	*ACS Catal.* **2018**, *8,* 4612
VOP NS	1 M KOH	1.51	72,000 s & 1,000 cycles (100%)	***This work***