Electronic Supplementary Information

Experimental section

Materials: $NiCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, NH_4F, HMT, KOH, and NaH_2PO_2 were purchased from Beijing Chemical Corp (China). Pt/C (20 wt% Pt on Vulcan XC-72R) and nafion (5 wt %) was purchased from Sigma-Aldrich. nickel foam was provided by Hongshan District, Wuhan Instrument Surgical Instruments Business. The ultrapure water used throughout all experiments through a Millipore system. All chemicals were used as received without further purification.

Preparation of hydroxide precursor : In a typical synthesis process, 3 mmol $NiCl_2 \cdot 6H_2O$, 1 mmol $MnCl_2 \cdot 4H_2O$, 5mmol NH_4F, 5 mmol HMT were dissolved in deionized water (30 mL) in a 50 mL beaker. After continuously stirring for 30 min, the solution was then transferred to a 50 mL Teflonlined stainless steel autoclave with a piece of nickel foam (2 cm × 3 cm). Then autoclave was sealed and maintained at 90 °C for 6 h in an oven. After the autoclave cooled down to room temperature, the hydroxide precursor was taken out and thoroughly washed with deionized water and ethanol several times alternatively, then dried at 60 °C for 6 h in air. Then the hydroxide precursor was obtained.

Preparation of Mn-Ni_2P nanosheet/NF: The hydroxide precursor was placed in an alumina boat and the other alumina boat containing 1.0 g NaH_2PO_2 was placed at the upstream of the tube furnace. The two alumina boats were calcined at 300 °C for 2 h with a heating speed of 2 °C min^{-1} under Ar flow and then cooled down to room temperature naturally. Ni_2P/NF were made, under otherwise identical conditions, without using $MnCl_2 \cdot 4H_2O$ for hydrothermal preparation.

Characterization: The XRD patterns were obtained from a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan).The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The scanning electron microscopy (SEM) were collected from the tungsten lamp-equipped SU3500 scanning electron microscope at an accelerating

voltage of 20 kV (HITACHI, Japan). The transmission electron microscopy (TEM) images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. ICP-MS analysis was performed on ThermoScientific iCAP6300.

Electrochemical measurement: The electrochemical measurements were performed on a CHI 660E electrochemical workstation (Chenhua, Shanghai). A three-electrode system was used in the experiment: a graphite rod was used as the counter electrode; a mercuric oxide electrode (Hg/HgO) was used as the reference electrode and the as-prepared Mn-Ni_2P/NF was used as the working electrode. All the measurements were performed at 298 K in 1.0 M KOH solution. The reference electrode was calibrated to the reversible hydrogen electrode (RHE): E (RHE) = E (Hg/HgO) + (0.098+ 0.059 pH) = E (Hg/HgO) + 0.924 V.

*TOF_{avg} calculation*s: The electrochemical active surface area (ECSA) is calculated using the following formula:[1]

$$A_{ECSA}^{Mn-Ni_2P} = \frac{C_{dl}}{40\ \mu F\ cm^{-2}\ per\ cm^2\ _{ECSA}}$$

To calculate the TOF_{avg}, we used the following formula:[1]

$$TOF_{avg} = \frac{\left(3.12 \times 10^{15} \times \frac{H_2/_S}{cm^2}\ per\ \frac{mA}{cm^2}\right) \times j}{2.001 \times 10^{15} \times A_{ECSA}}$$

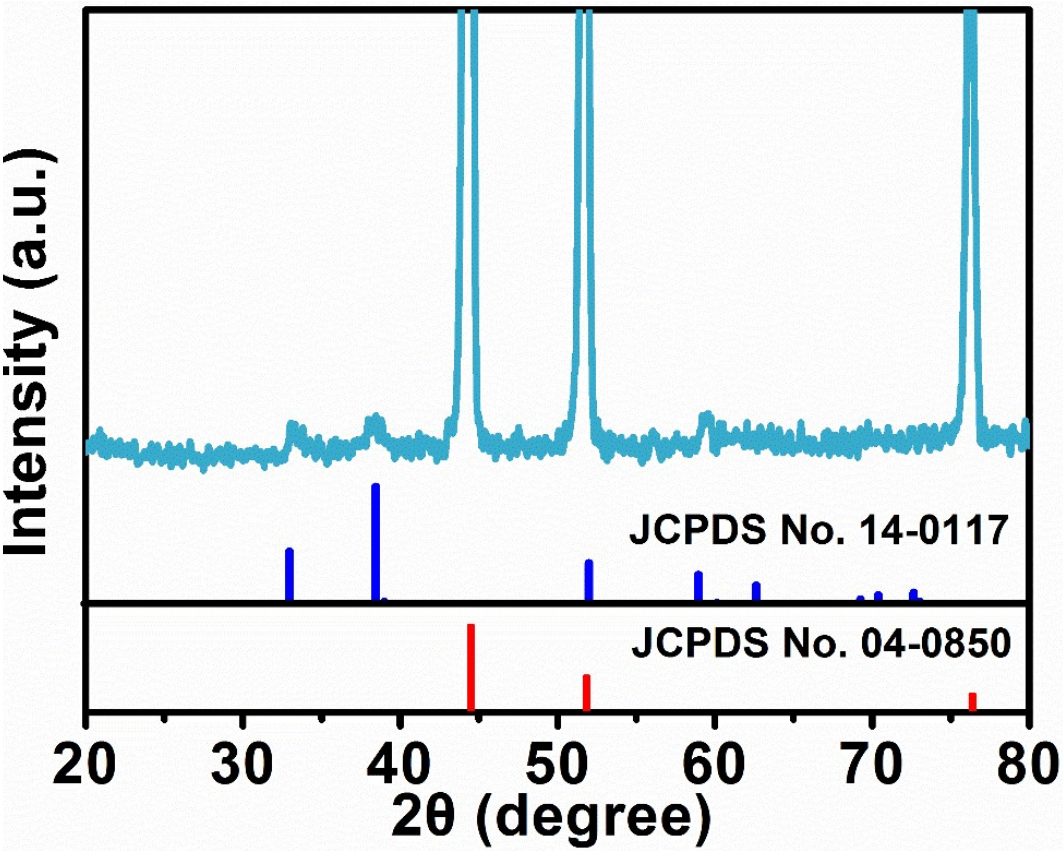

Fig. S1. XRD pattern of hydroxide precursor.

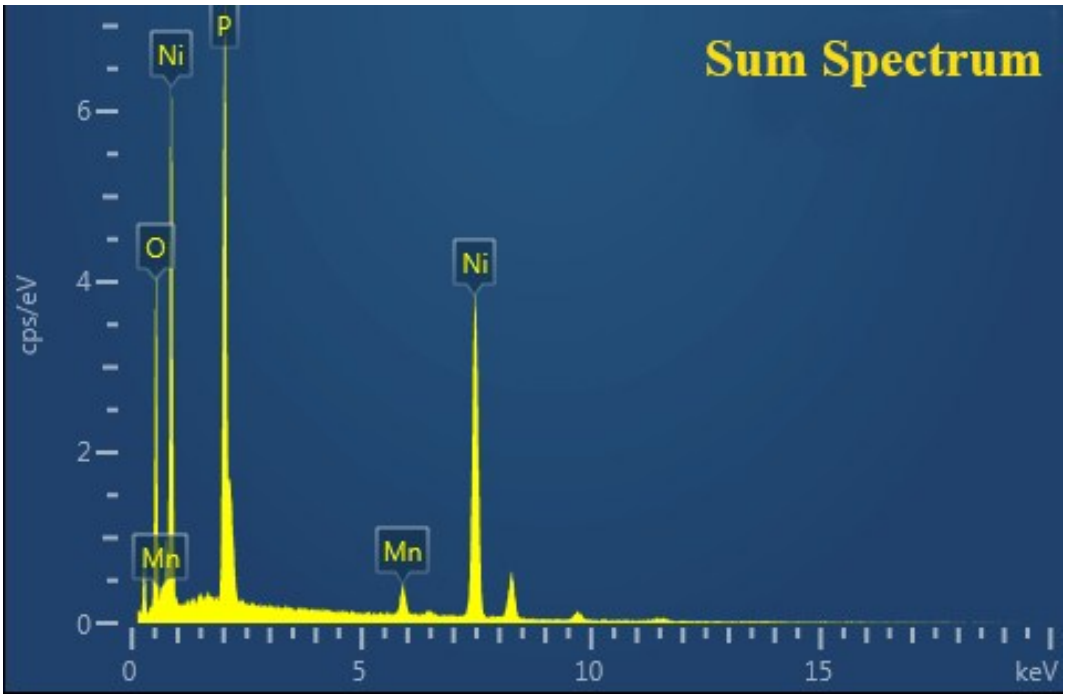

Fig. S2. EDX spectrum of Mn-Ni_2P/NF.

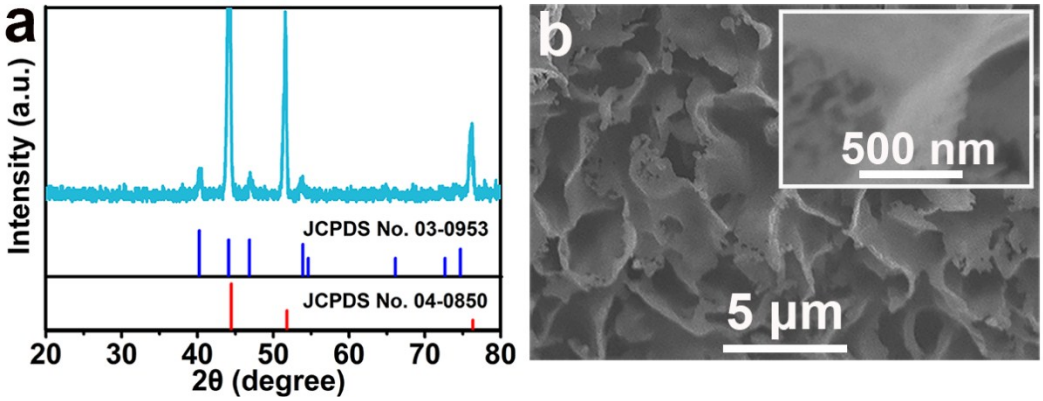

Fig. S3. (a) XRD pattern and (b) SEM images of Ni_2P/NF

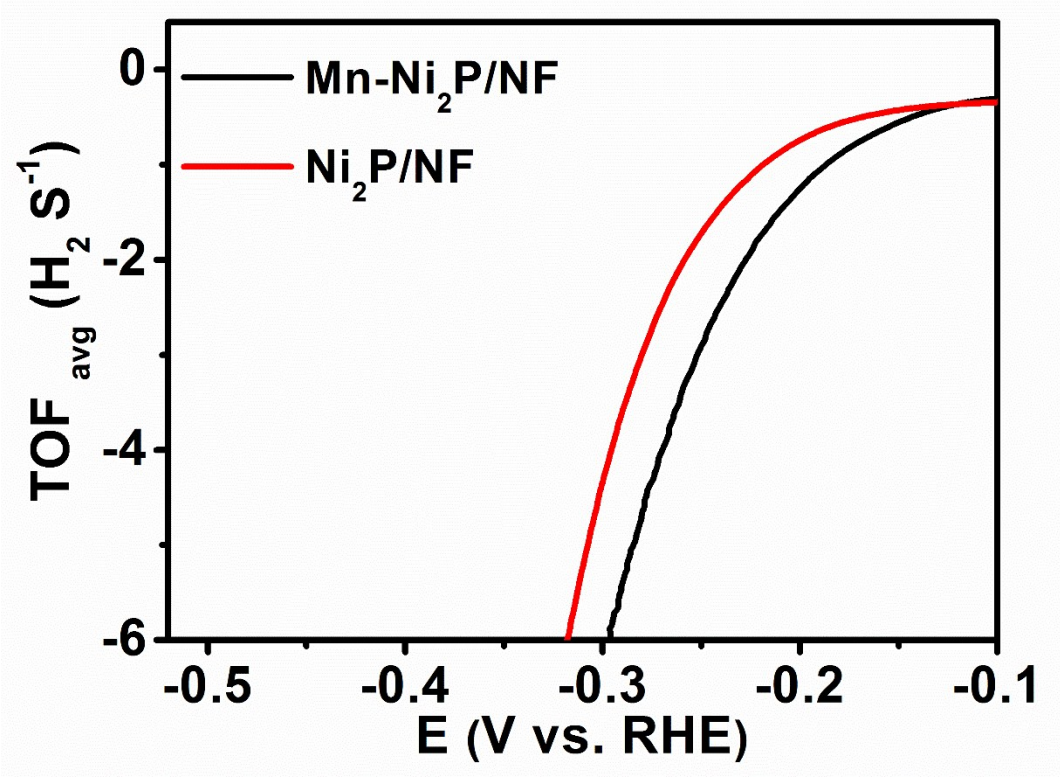

Fig. S4. TOF_{avg} calculation of Mn-Ni_2P/NF and Ni_2P/NF.

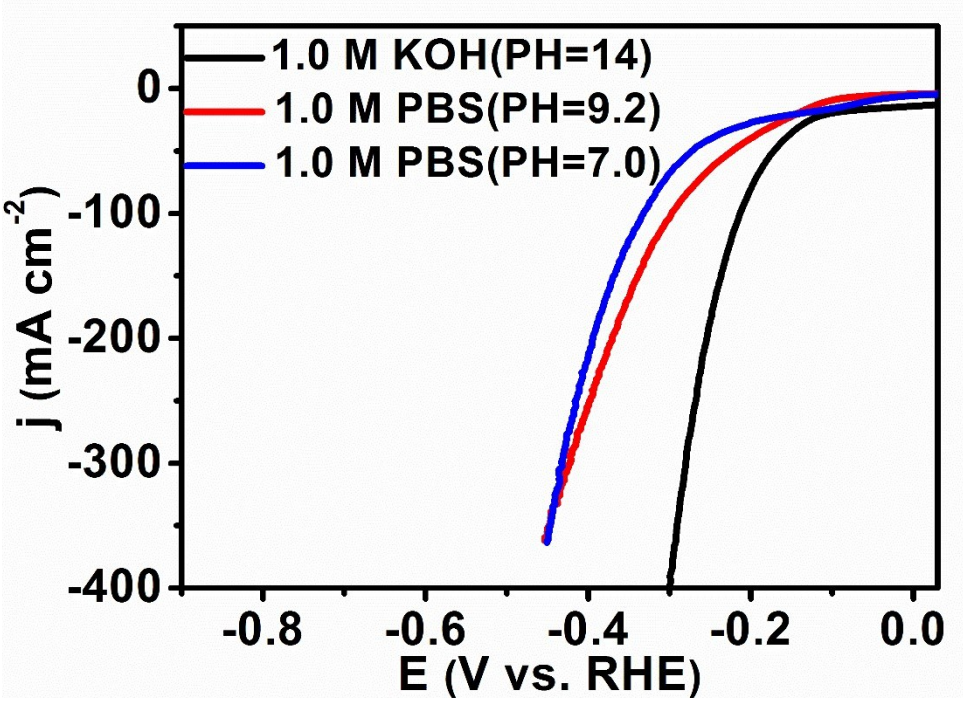

Fig. S5. LSV curves for Mn-Ni_2P/NF in PH=7.0, 9.2, 14 with a scan rate of 5 mVs^{-1} for HER with iR correction

Table S1. Comparison of HER performance for Mn-Ni_2P/NF with other non-noble-metal electrocatalysts at 1.0 M KOH

Catalyst	j (mA cm^{-2})	η (mV)	Reference
Mn-Ni_2P/NF	20	103	This work
porous Ni/Ni_3S_2	20	115	2
MoCx/C	20	>175	3
H_2-CoCat	10	>-385	4
CoOx@CN	10	270	5
MoS_{2+x}/FTO	10	310	6
CoP/CC	10	209	7
Co-NRCNTs	20	>450	8
MoB	10	>225	9
Ni_3N	10	208	10
NiMoN	10	109	
CoP/rGO-400	10	340	11
Ni_3N/NF	10	121	12
Ni wire	10	350	13
NiS_2/CC	10	149	14
WP_2 submicroparticles	10	153	15
NiFe-LDH/NF	10	250	16
FeP NAs/CC	10	218	17
FeP/Fe foil	10	194	18
CFP-FeP HNA	10	181	19
Co_2P nanorods	20	171	20
Porous Co-P film	20	410	21
Ni_5P_4 nanosheets on Ni foil	10	150	22

WP nanorods/CC	10	150	23
Ni_2P NSs/CC	20	250	24
Ni_2P/NF	15	185	25
MoP/Ni_2P/NF	20	110	26

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