Electronic Supplementary Information

Experimental section

Materials: $Ni(NO_3)_2·6H_2O$, $Al(NO_3)_3·9H_2O$, NH_4F, urea and NaH_2PO_2 were purchased from Beijing Chemical Corp. (China). Pt/C (20 wt% Pt on Vulcan XC-72R) was purchased from Sigma-Aldrich. Ti mesh 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, 10 mmol $Ni(NO_3)_2·6H_2O$, 1 mmol $Al(NO_3)_3·9H_2O$, 16 mmol NH_4F and 40 mmol urea were dissolved in 80 mL deionized water under vigorous stirring for 30 min. Then the solution was transferred to a 100 mL Teflonlined stainless steel autoclave with a piece of Ti mesh (3 cm × 4 cm). Then autoclave was sealed and maintained at 120 °C for 10 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, then dried at 60 °C for 6 h in air. Then the NiAl-LDH/TM was obtained. The hydroxide precursor of Ni_2P/TM were made under the same conditions without using $Al(NO_3)_3·9H_2O$.

Preparation of Al-Ni_2P/TM and Ni_2P/TM: 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 flowed and then cooled down to room temperature naturally. Ni_2P/TM was made under identical conditions.

Preparation of Pt/C electrode: To prepare Pt/C electrode, 20 mg Pt/C and 10 μL Nafion solution (5 wt%) were dispersed in 1 mL water/ethanol (v:v=1:1) solvent by 30 min sonication to form an ink finally. Then 63 μL catalyst ink was loaded on bare TM with a catalyst loading of 1.25 mg cm^{-2}.

Characterization: The X-ray diffraction (XRD) patterns were obtained from a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40kV, 30mA) of wavelength

0.154 nm (SHIMADZU, Japan). Scanning electron microscope (SEM) measurements were recorded on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. The structures of the samples were determined by Transmission electron microscopy (TEM) images on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) data of the samples was collected on an ESCALABMK II x-ray photoelectron spectrometer using Mg as the exciting source. Inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis was performed on ThermoScientific IAP6300.

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 mercuric oxide electrode (Hg/HgO) was used as the reference electrode, a graphite rod was used as the counter electrode and the as-prepared Al-Ni_2P/TM was used as the working electrode. All tests were carried out at room temperature. The potentials reported in this work were calibrated to RHE other than especially explained, using the following equation: E (RHE) = E (Hg/HgO) + (0.098 + 0.059 × pH) V.

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

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

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

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

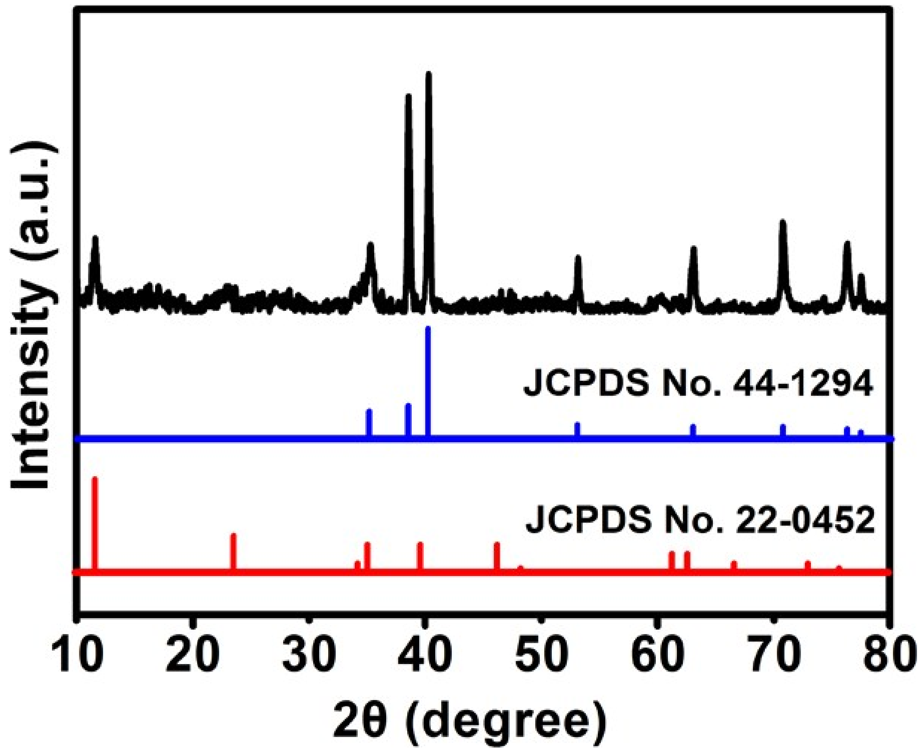

Fig. S1. XRD pattern of NiAl-LDH/TM.

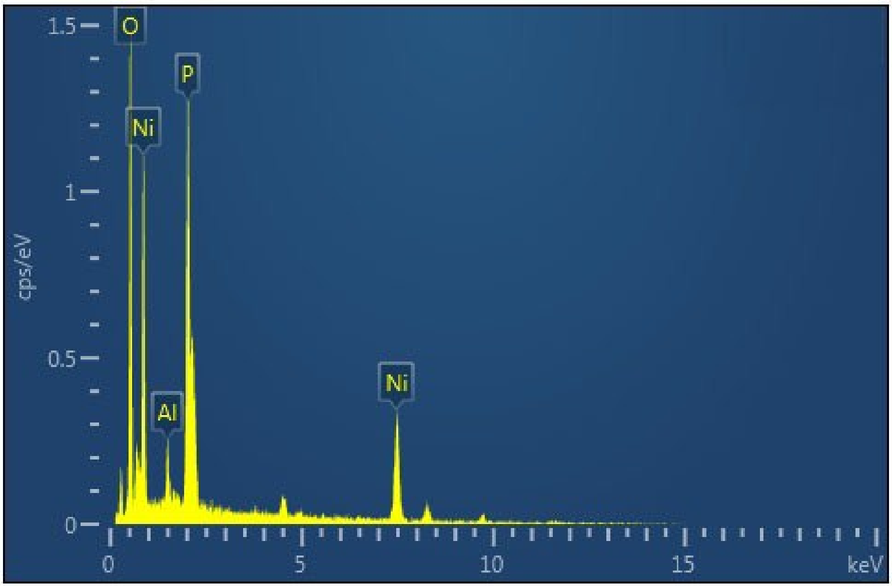

Fig. S2. EDX spectrum for Al-Ni_2P/TM.

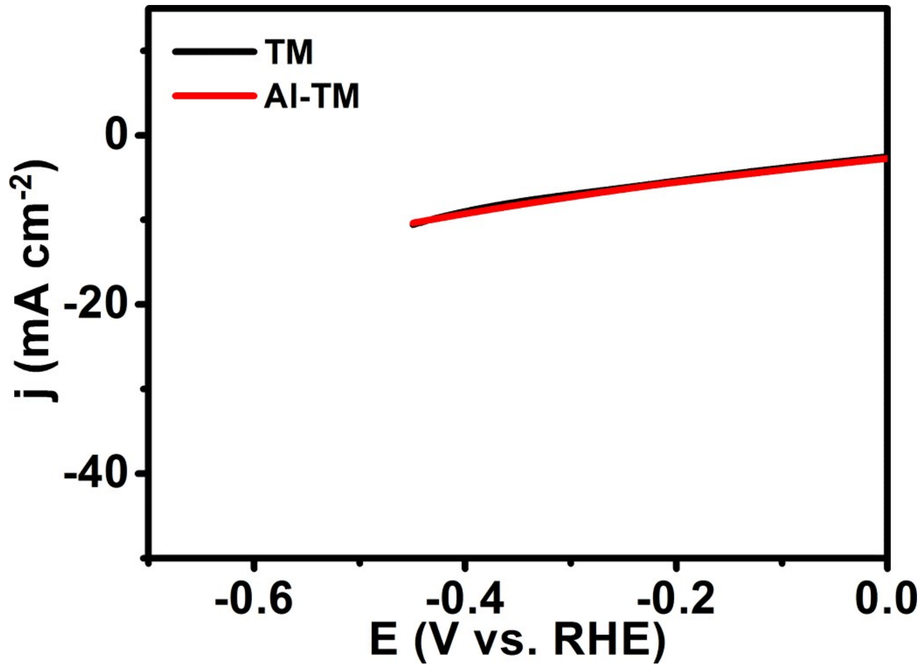

Fig. S3. LSV curves for bare TM and Al-TM.

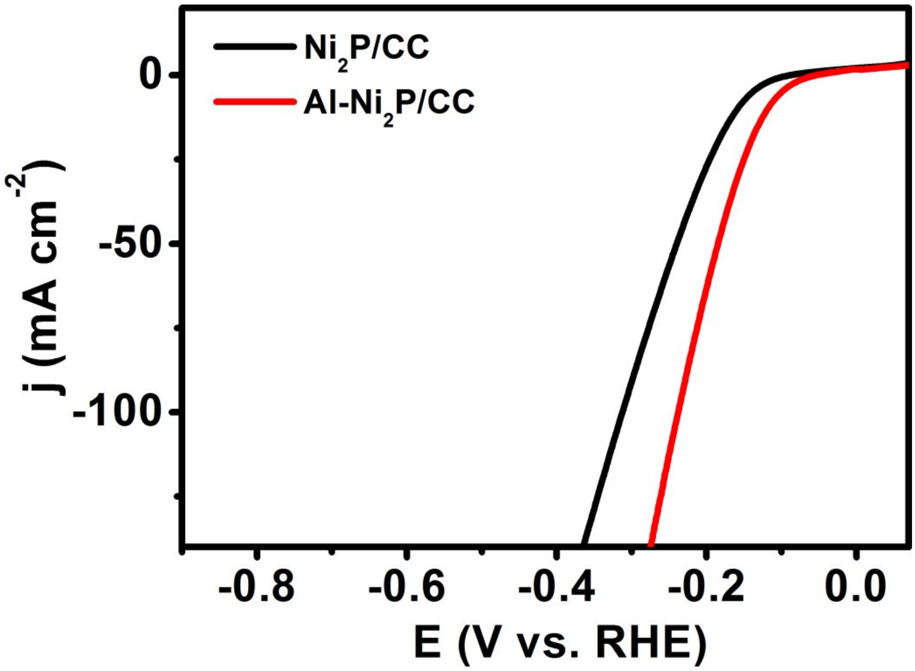

Fig. S4. LSV curves for Ni_2P/CC and Al-Ni_2P/CC in 1.0 M KOH.

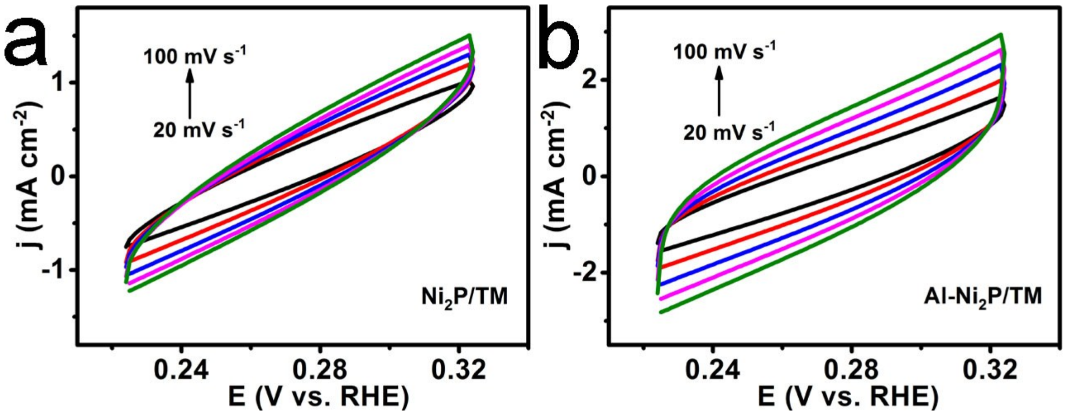

Fig. S5. CVs of (a) Ni_2P/TM and (b) Al-Ni_2P/TM with various scan rates in the region from 0.224 to 0.324 V.

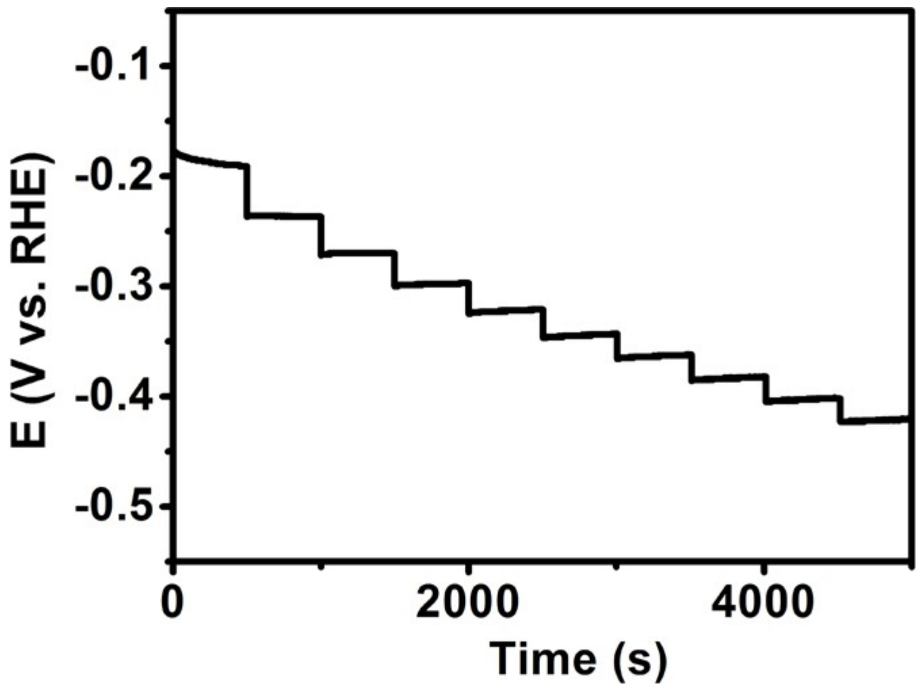

Fig. S6. Multi-current process of Al-Ni_2P/TM without iR correction. The current density started at 20 mA cm^{-2} and ended at 200 mA cm^{-2}, with an increment of 20 mA cm^{-2} per 500 s.

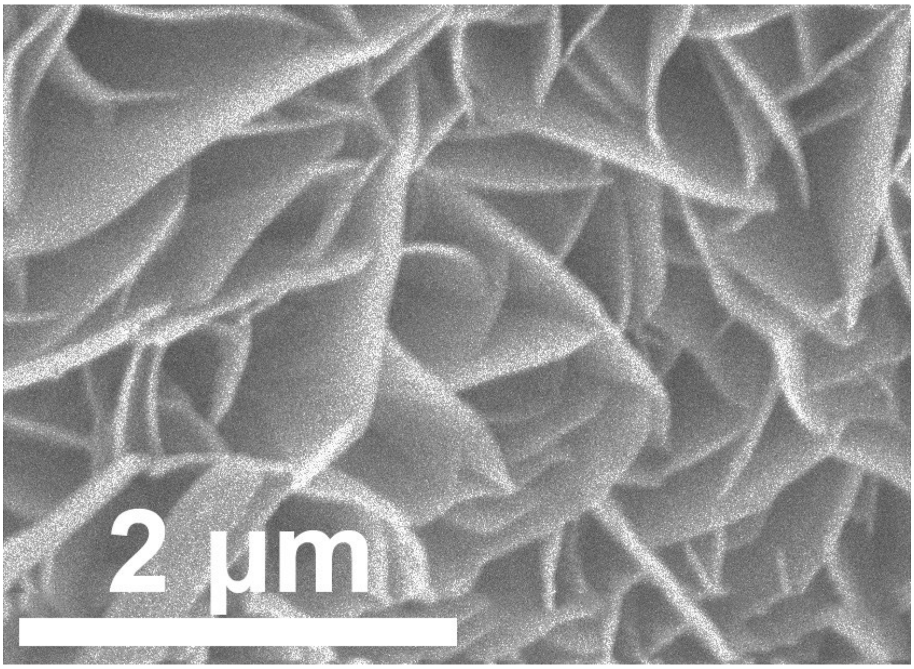

Fig. S7. SEM image of Al-Ni_2P/TM after stability test.

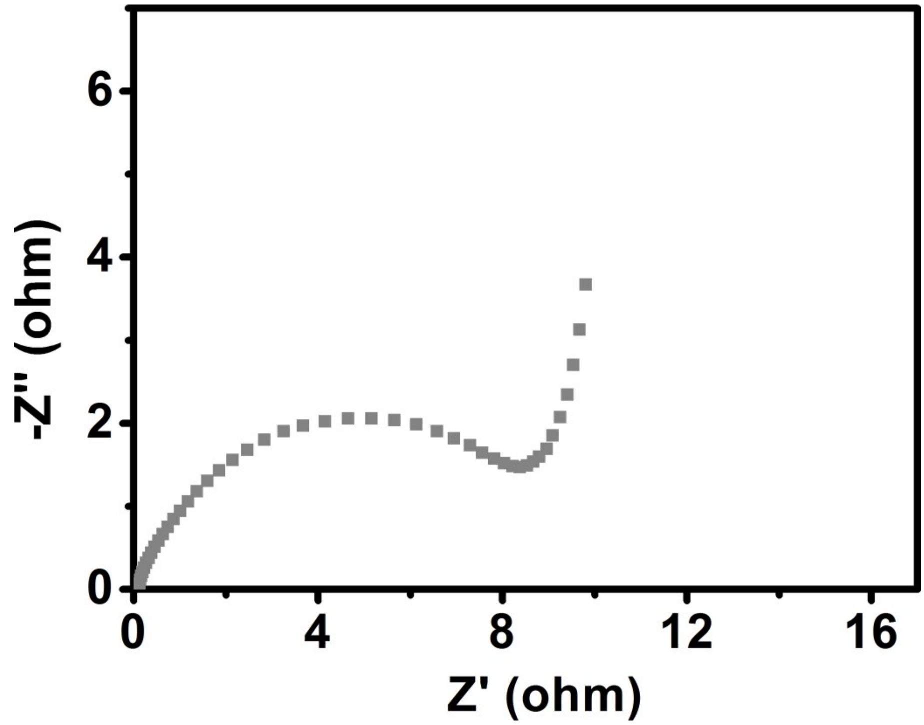

Fig. S8. Nyquist plots of Al-Ni_2P/TM after stability test.

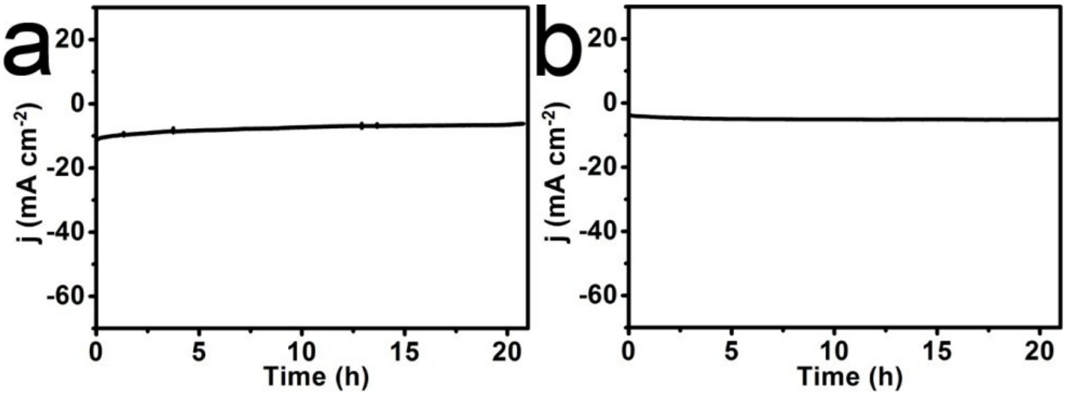

Fig. S9. Time-dependent current density curves of (a) Ni_2P/TM and (b) Al-TM.

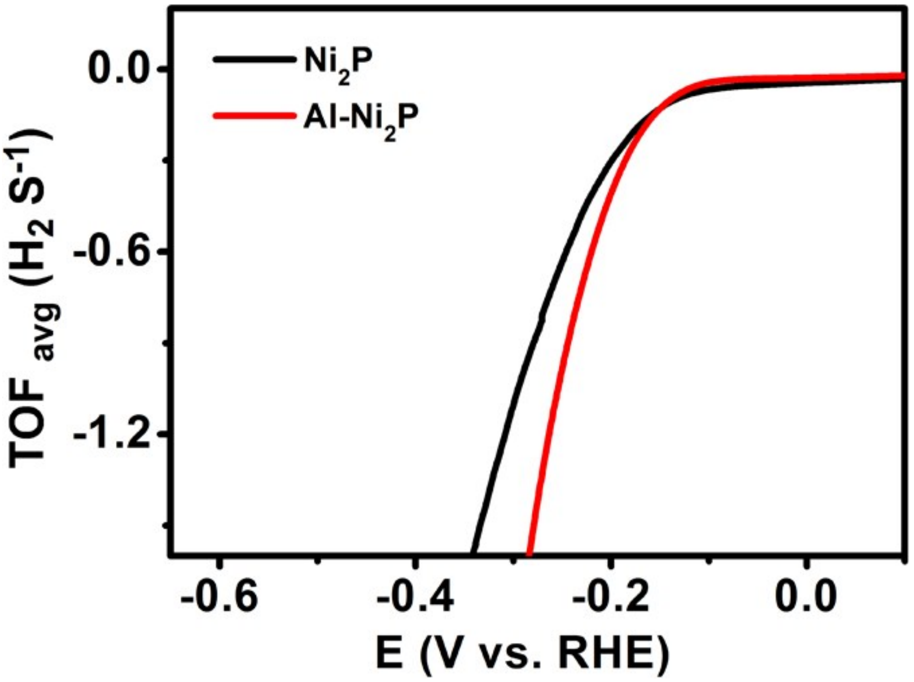

Fig. S10. TOF_{avg} calculation of Ni_2P/TM and Al-Ni_2P/TM.

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

Catalyst	*j* (mA cm^{-2})	*η* (mV)	Stability test (h)	Reference
Al-Ni_2P/TM	10	129	20	This work
Ni_2P/TM	10	176		
NiFe-LDH/NF	10	210	--	2
Ni_2P nanoparticles	10	~220	48	3
Ni_3S_2 nanosheet/NF	10	223	200	4
CoP/CC	10	209	22	5
MoS_2/Mo	10	184	17	6
Ni-P	10	350	--	7
Ni_2P-mesoG	10	188	23	8
Ni_2P/mesoG	10	256	--	
Ni_2P nanoparticles	10	220	10	9
FeP NAs/CC	10	218	20	10
$NiCo_2S_4$ NA/CC	50	263	12	11

Table S2. ICP-AES data for the electrolyte after the electrochemical durability.

	Al (μg mL^{-1})	Ni (μg mL^{-1})	P (μg mL^{-1})
Sample	0.51	0.11	0.20

References

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