Electronic Supplementary Information

Experimental section

Materials: Ti mesh (TM) was provided by Hangxu Filters Flag Store, Hengshui, Hebei. The $FeCl_3 \cdot 6H_2O$, urea, and sodium hypophosphite (NaH_2PO_2), was purchased from Aladdin Ltd. in Shanghai. Pt/C (20 wt% Pt on Vulcan XC-72R) and 5 wt% Nafion, was purchased from Alfa Aesar (China) Chemicals Co. Ltd. The water used throughout all experiments was purified through a Millipore system. All the reagents and chemicals were used as received without further purification.

Preparation of FeOOH/TM and Fe_2P/TM: FeOOH/TM and Fe_2P/TM was prepared as follows. 2.702 g $FeCl_3 \cdot 6H_2O$ and 0.9 g urea were dissolved in 100 mL ultrapure water under magnetic stirring to form a uniform solution. We chose Ti mesh as the substrate due to its excellent chemical stability, acceptable electronic conductivity, three dimensional structure with high surface area, and open structure allowing solvent good access at the reaction interface.[1,2] Ti mesh was cleaned by sonication in water and ethanol for 10 min, was immersed into the solution. Then, the pre-treated Ti mesh (2 × 3 cm) and the above solution were transferred into a 100 mL Teflon-lined stainless-steel autoclave and maintained at 100℃ for 4 h. After cooled to room temperature, the product was washed with ultrapure water for three times. Then the FeOOH/TM was obtained. To prepare Fe_2P/TM, FeOOH and 500 mg NaH_2PO_2 were put a porcelain boat with NaH_2PO_2 at the bottom of the porcelain. Subsequently, the samples were heated at 300 °C for 2 h in a flow Ar atmosphere.

Preparation of $Ni(OH)_2$-Fe_2P/TM: The electrodeposition of $Ni(OH)_2$ on Fe_2P/TM was carried out in a standard three electrode electrochemical cell (as-obtained Fe_2P/TM, working electrode; graphite plate, counter electrode; saturated calomel electrode, reference electrode). The electrolyte was an aqueous solution of 0.1 M $NiCl_2$. The electrodeposition experiments were all carried out at a constant cathodic potential of -1.0 V for 100 s. After the deposition, the obtained composite electrode was taken out, rinsed with deionized water several times and dried at 60 °C in air. The loading for $Ni(OH)_2$ on Fe_2P/TM was about 1.34 mg cm^{-2}.

Synthesis of Pt/C: To prepare Pt/C electrode, 50 mg Pt/C and 20 μL 5 wt% Nafion solution and 280 μL ethanol were dispersed in 700 μL water by 30 min sonication to form an ink finally. Then 6.7 μL catalyst ink was loaded on bare TM (0.5 × 0.5 cm) with a catalyst loading of 1.34 mg cm^{-2}.

Characterizations: 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). 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.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system. $Ni(OH)_2$-Fe_2P/TM was used as the working electrode. Graphite plate, and an Hg/HgO were used as the counter electrode and the reference electrode, respectively. The temperature of solution was kept at 25 °C for all the measurements via the adjustment of air condition and heating support, which ensured the variation of diffusion coefficient below 1%. 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.

FE determination: The FE was calculated by comparing the amount of measured H_2 generated by cathodal electrolysis with calculated H_2 (assuming 100% FE). GC analysis was carried out on GC–2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. Pressure data during electrolysis were recorded using a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of 1 point per second.

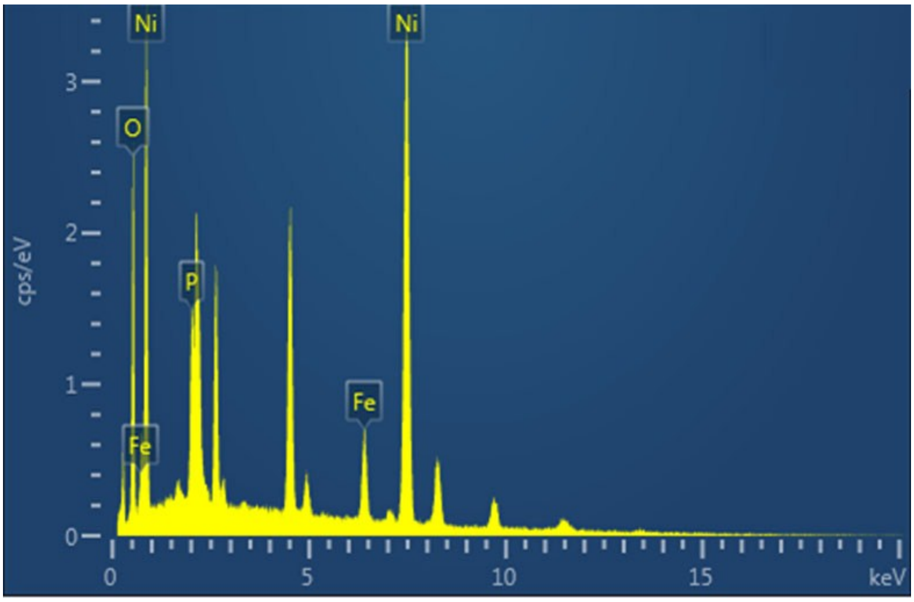

Fig. S1. EDX spectrum of $Ni(OH)_2$-Fe_2P/TM.

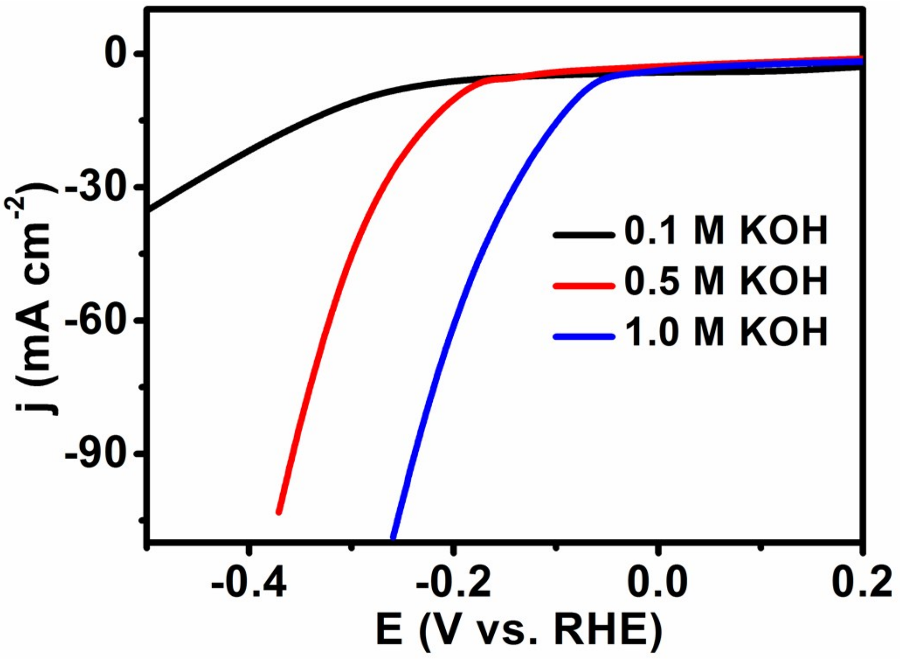

Fig. S2. LSV curves of $Ni(OH)_2$-Fe_2P/TM in different concentrations.

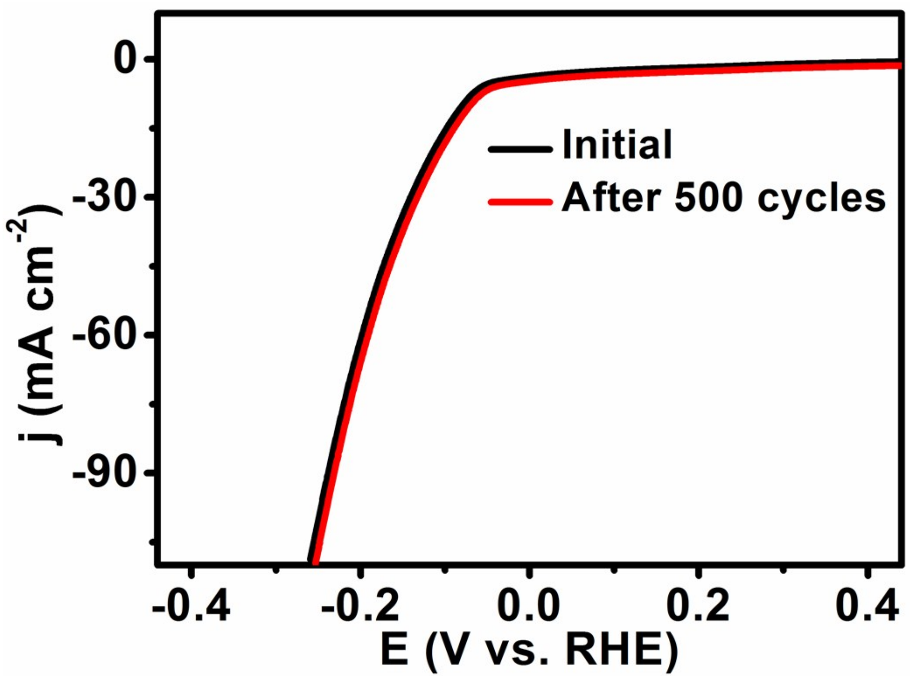

Fig. S3. LSV curves of Ni(OH)$_2$-Fe$_2$P/TM before and after 500 cycles.

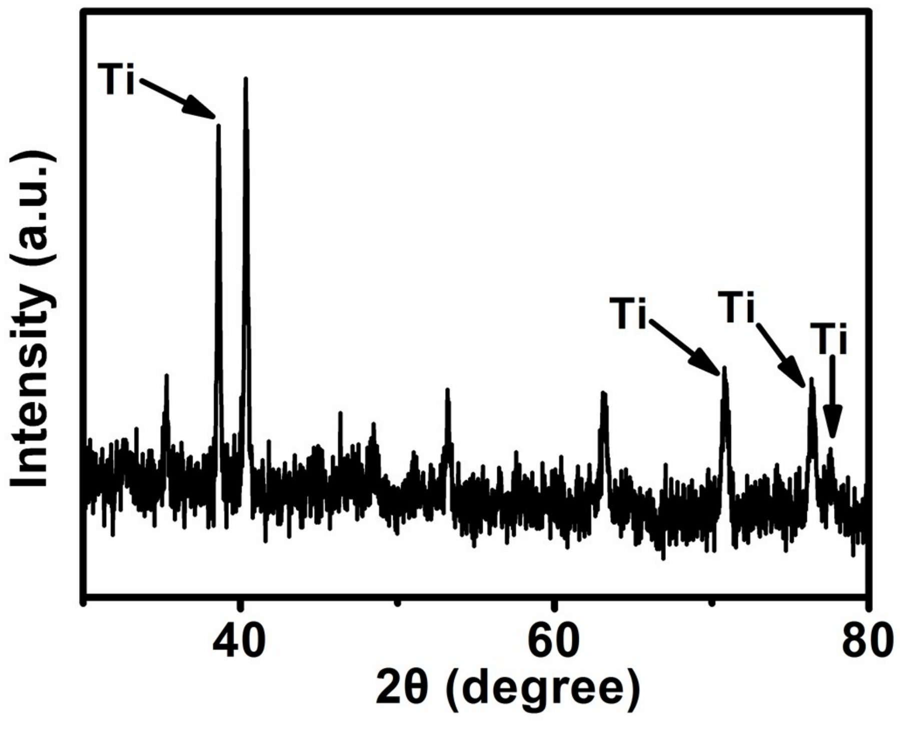

Fig. S4. The XRD pattern of Ni(OH)$_2$-Fe$_2$P/TM after stability test.

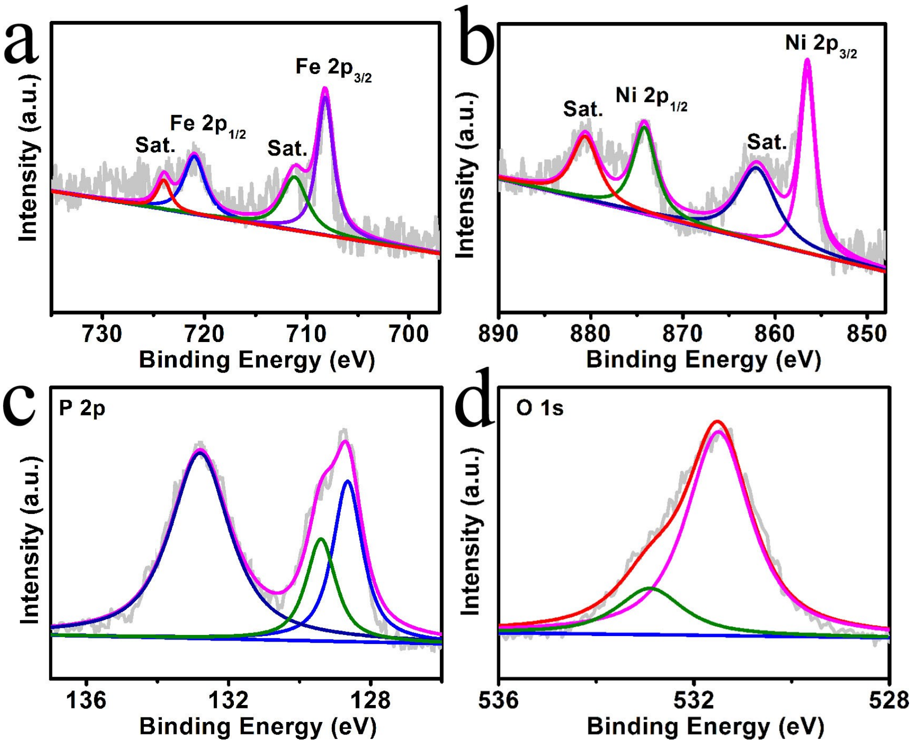

Fig. S5. XPS spectra of $Ni(OH)_2$-Fe_2P in the (a) Fe 2p, (b) Ni 2p, (c) P 2p, and (d) O 1s regions after stability test.

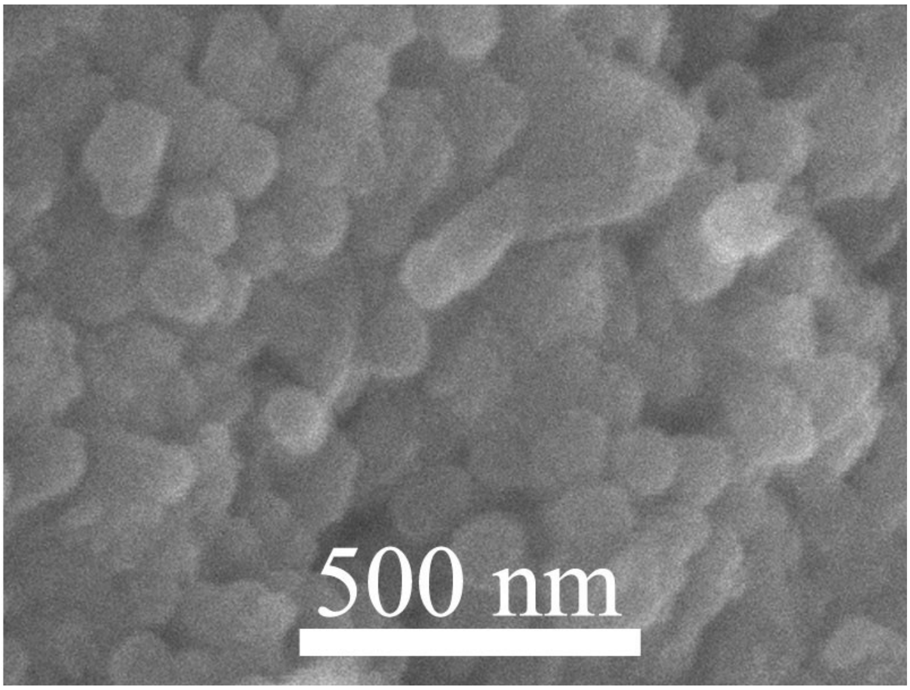

Fig. S6. The SEM image of $Ni(OH)_2$-Fe_2P/TM after stability test.

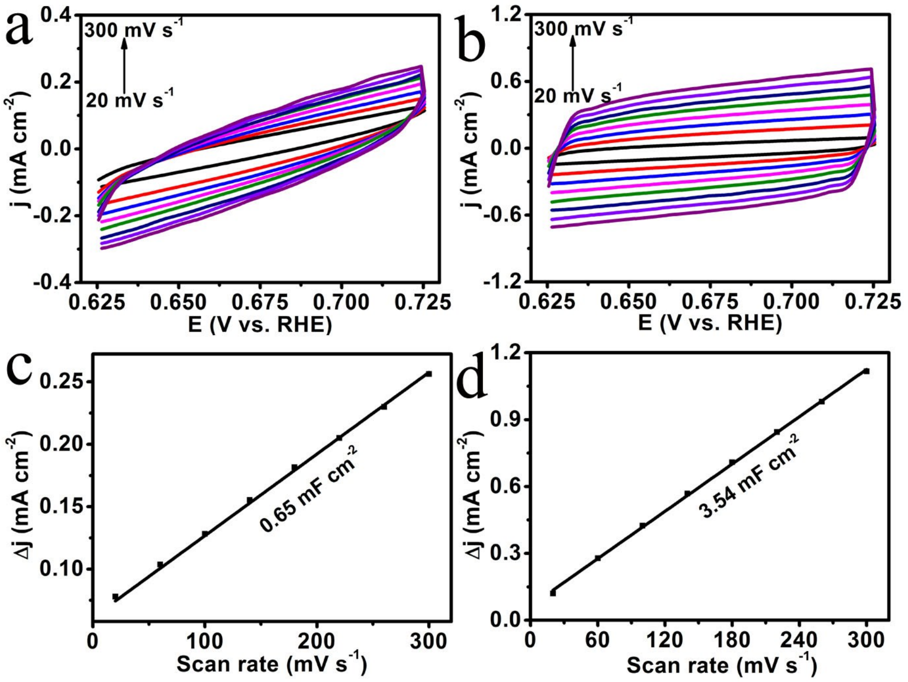

Fig. S7. CVs for (a) Fe_2P/TM and (b) $Ni(OH)_2$-Fe_2P/TM in the non-faradaic capacitance current range at scan rates of 20, 60, 100, 140, 180, 220, 260 and 300 mV s^{-1}. (c ,d) Corresponding capacitive current of scan rates for Fe_2P/TM and $Ni(OH)_2$-Fe_2P/TM in 1.0 M KOH, respectively.

Table S1. Comparison of HER performance for $Ni(OH)_2$-Fe_2P/TM with other non-noble-metal electrocatalysts in alkaline media.

Catalyst	j (mA cm^{-2})	η (mV)	Electrolyte	Ref.
$Ni(OH)_2$-Fe_2P/TM	10	76	1.0 M KOH	This work
Fe_2P/TM	10	170	1.0 M KOH	
FeP array	10	194	1.0 M KOH	3
FeP_2 array	10	189	1.0 M KOH	
FeP NAs/CC	10	218	1.0 M KOH	4
CoP/CC	10	209	1.0 M KOH	5
NiFeS/NF	10	180	1.0 M KOH	6
Fe_2P/NGr	20	376	1.0 M KOH	7
Ni_2P	10	220	1.0 M KOH	8
Cu_3P@NF	10	105	1.0 M NaOH	9
Cu_3P NB/Cu	10	252	1.0 M KOH	10
Mo-Ni_2P	10	78	1.0 M KOH	11
Ni_2P@mesoG	10	188	1.0 M KOH	12
Ni_2P/mesoG	10	256	1.0 M KOH	
O-Co_2P-3	10	160	1.0 M KOH	13

References

1. E. Szabados, G. Sagi, F. Somodi, B. Maroti, D. Sranko and A. Tungler, *J. Ind. Eng. Chem.*, 2017, **46**, 364–372
2. H. Cheng and K. Scott, *J. Appl. Electrochem.*, 2006, **36**, 1361–1366.
3. C. Y. Son, I. H. Kwak, Y. R. Lim and J. Park, *Chem. Commun.,* 2016, **52,** 2819–2822.
4. Y. Liang, Q. Liu, A. M. Asiri, X. Sun and Y. Luo, *ACS Catal.,* 2014, **4**, 4065–4069.
5. J. Tian, Q. Liu, A. M. Asiri and X. Sun, *J. Am. Chem. Soc.,* 2014, **136,** 7587–7590.
6. P. Ganesan, A. Sivanantham and S. Shanmugam, *J. Mater. Chem. A,* 2016, **4**, 16394–16402.
7. Z. Huang, C. Lv, Z. Chen, Z. Chen, F. Tian and C. Zhang, *Nano Energy,* 2015, **12,** 666–674.
8. L. A. Stern, L. Feng, F. Song and X. Hu, *Energy Environ. Sci.,* 2015, **8**, 2347–2351.
9. A. Han, H. Zhang, R. Yuan, H. Ji and P. Du, *ACS Appl. Mater. Interfaces*， 2017, **9,** 2240–2248.
10. S. Wei, K. Qi, Z. Jin, J. Cao, W. Zheng, H. Chen and X. Cui, *ACS Omega,* 2016, **1,** 1367–1373.
11. Y. Sun, L. Hang, Q. Shen, T. Zhang, H. Li, X. Zhang, X. Lyu and Y. Li, *Nanoscale,* 2017, **9**, 16674–16679.
12. S. Jeoung, B. Seo, J. M. Hwang, S. H. Joo and H. R. Moon, *Mater. Chem. Front.*, 2017, **1**, 973–978.
13. K. Xu, H. Ding, M. Zhang, M. Chen, Z. Hao, L. Zhang, C. Wu and Y. Xie, *Adv. Mater.,* 2017, **29**, 1606980.