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Supplementary Information

Phosphorized polyoxometalate-etched iron-hydroxide porous nanotubes for efficient electrocatalytic oxygen evolution

Hong Lin,[a] Jia-Wei Wang,[a] Xiang-Wei Guo,[a] Shuang Yao,[,b] Meng Liu,[a] Zhi-Ming Zhang,*[,a] and Tong-Bu Lu[a]*

[a]Institute for New Energy Materials and Low Carbon Technologies, School of Material Science & Engineering, Tianjin University of Technology, Tianjin 300384, People's Republic of China.

[b]Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, People's Republic of China.

*Email: shuangyao@email.tjut.edu.cn, zmzhang@email.tjut.edu.cn

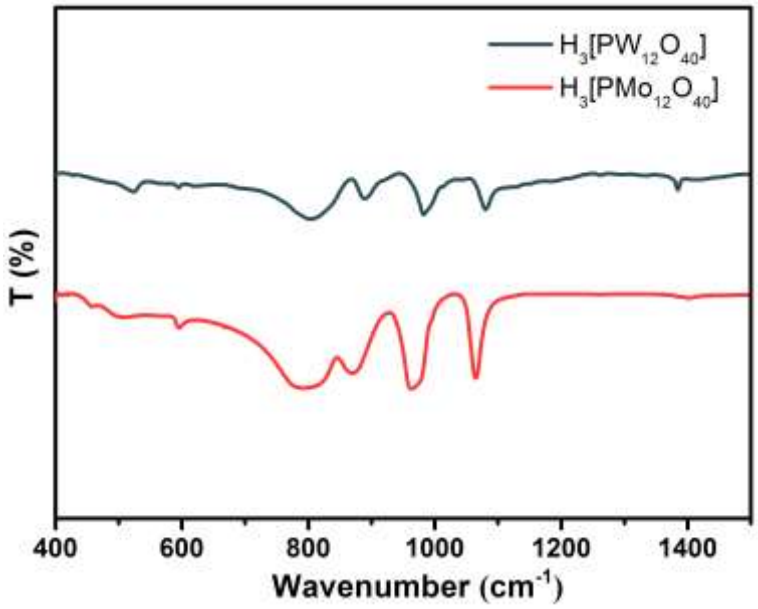

Fig. S1 FT-IR spectra of $H_3[PW_{12}O_{40}]$ and $H_3[PMo_{12}O_{40}]$.

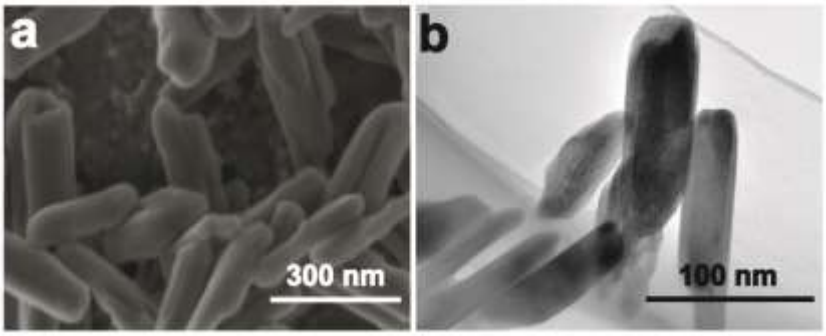

Fig. S2 (a) SEM and (b) TEM images of PMo_{12}-Fe-O nanotubes.

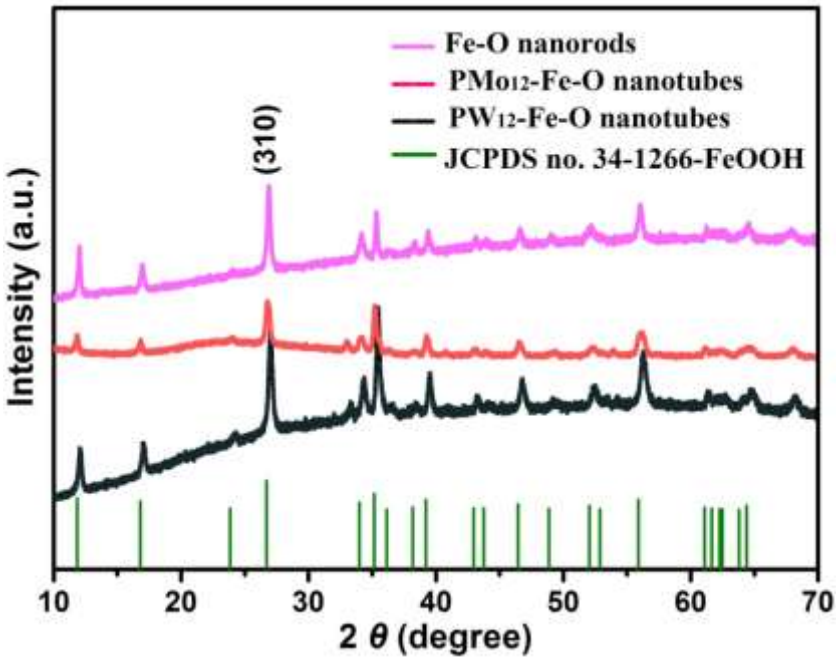

Fig. S3 XRD patterns of PW_{12}-Fe-O, PMo_{12}-Fe-O and Fe-O samples as well as the standard XRD pattern of β-FeOOH.

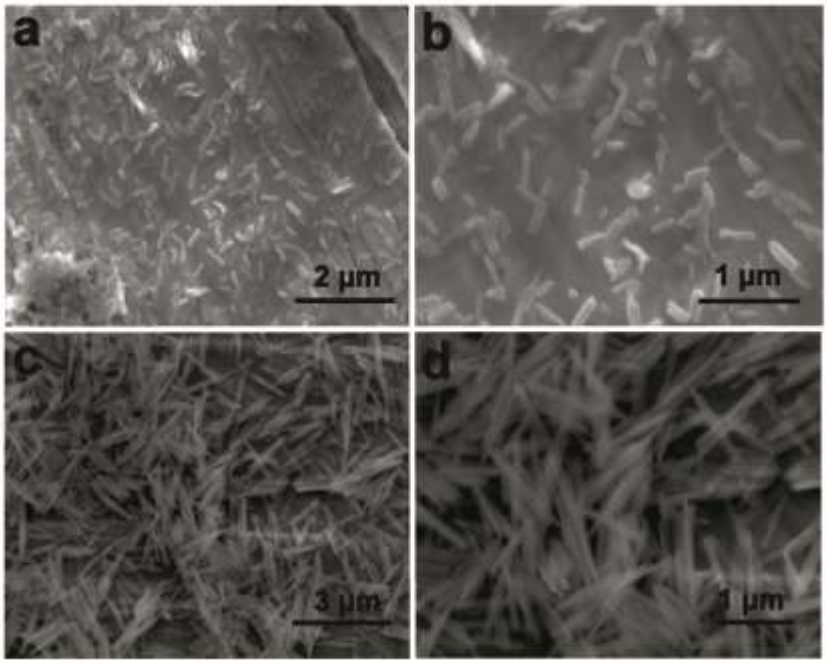

Fig. S4 SEM images of (a, b) PW_{12}-Fe-O nanotubes and (c, d) Fe-O nanorods.

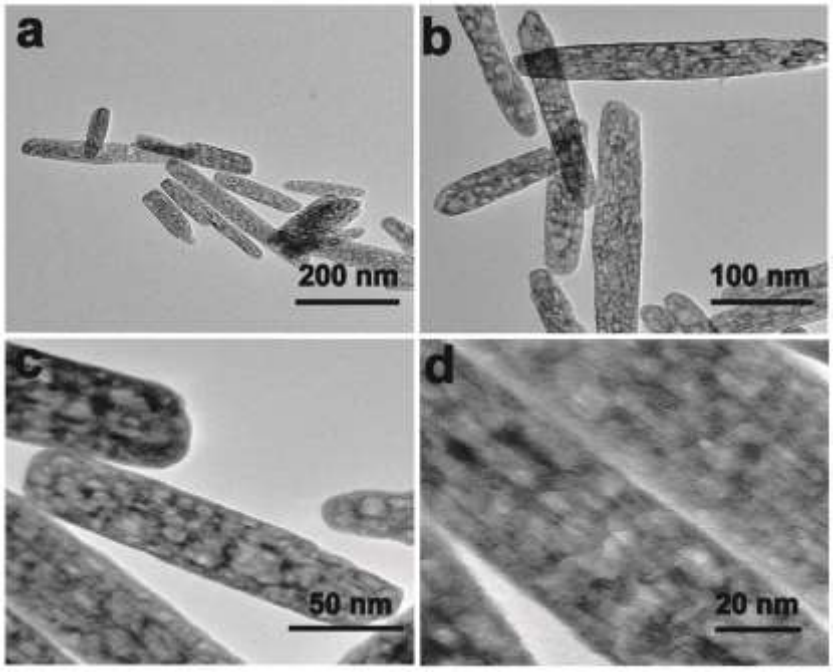

Fig. S5 TEM images of PW_{12}-Fe-P nanotubes.

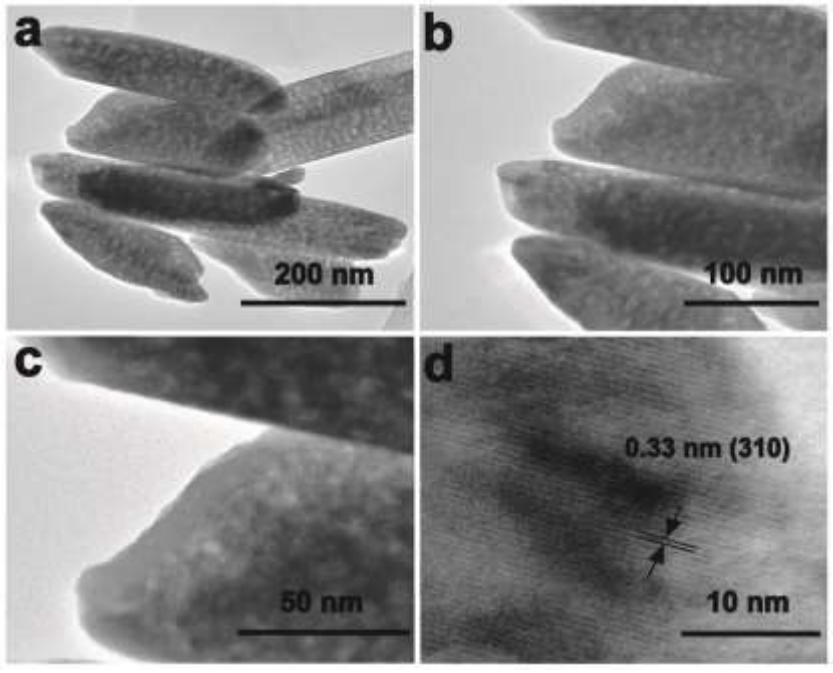

Fig. S6 TEM images of PMo_{12}-Fe-P nanotubes.

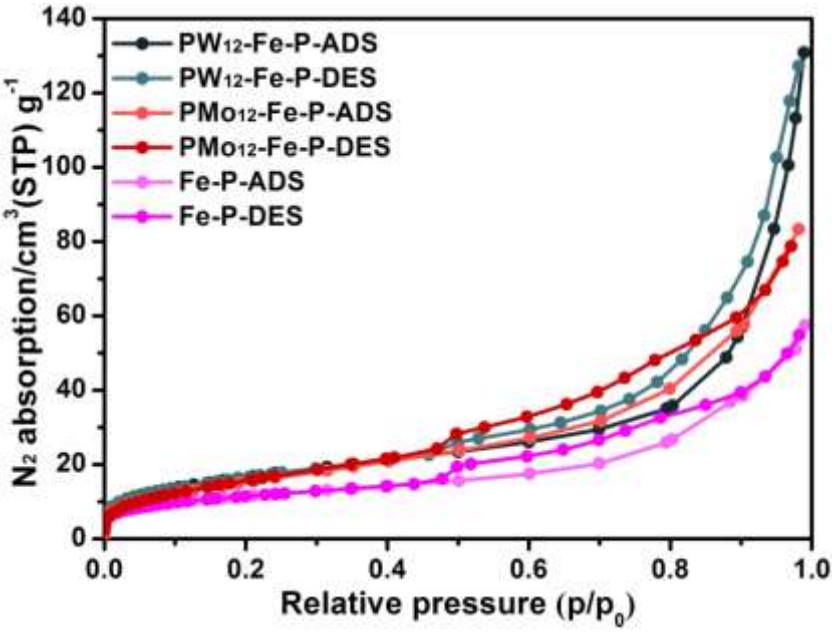

Fig. S7 N_2 sorption isotherms of PW_{12}-Fe-P, PMo_{12}-Fe-P and Fe-P samples at 77 K.

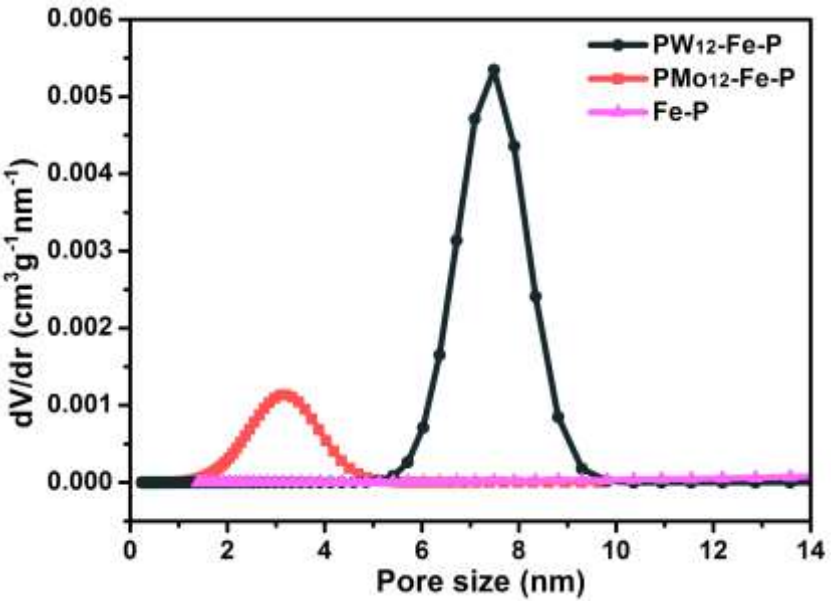

Fig. S8 Pore size distribution of PW_{12}-Fe-P, PMo_{12}-Fe-P and Fe-P.

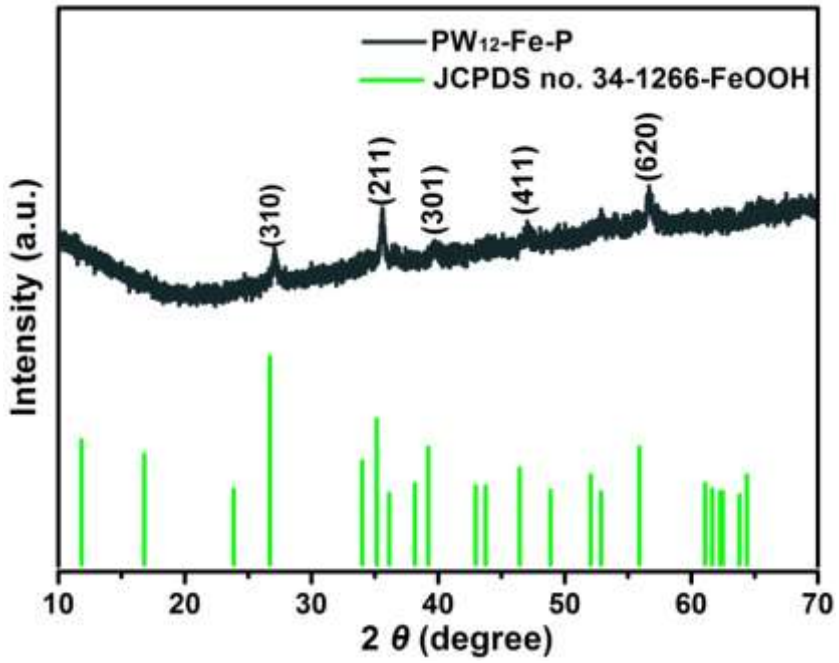

Fig. S9 XRD patterns of PW_{12}-Fe-P nanotubes and the standard XRD pattern of β-FeOOH.

Table S1. ICP-MS results of PW_{12}-Fe-P nanotubes.

Samples	Fe (wt%)	W (wt%)
PW_{12}-$Fe(PO_3)_3$	20.8318	0.0959
	23.3528	0.2192
	22.2744	0.1501
Average value	22.1530	0.1551

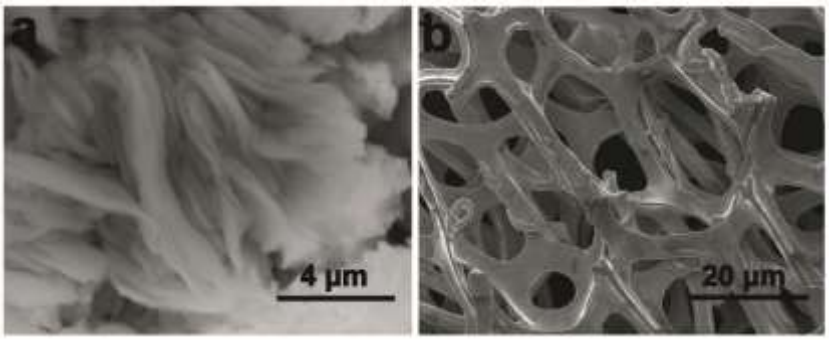

Fig. S10 SEM images of (a) NF-P and (b) NF.

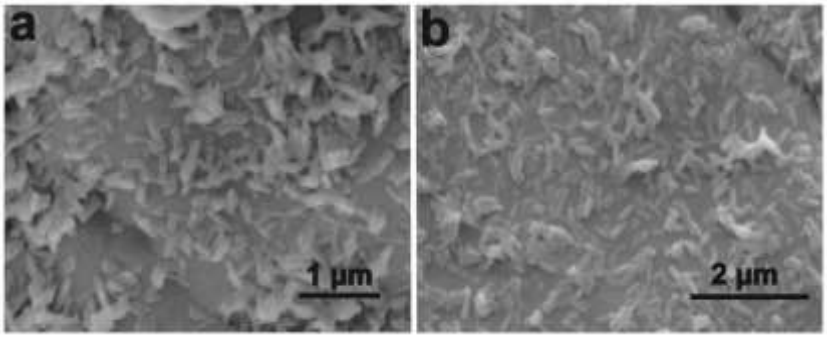

Fig. S11 SEM images of PW_{12}-Fe-P@NF-P (a) before and (b) after OER tests.

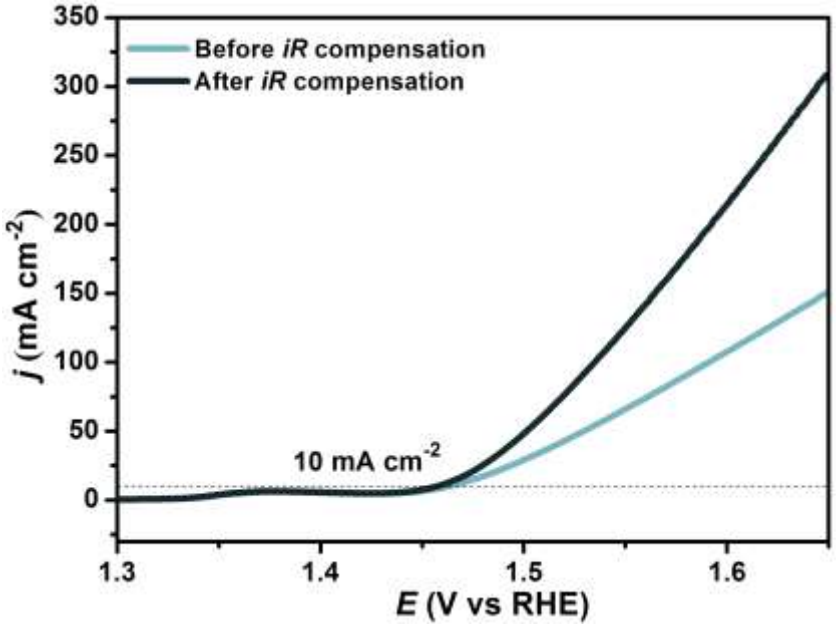

Fig. S12 The polarization curves before and after iR compensation for PW_{12}-Fe-P.

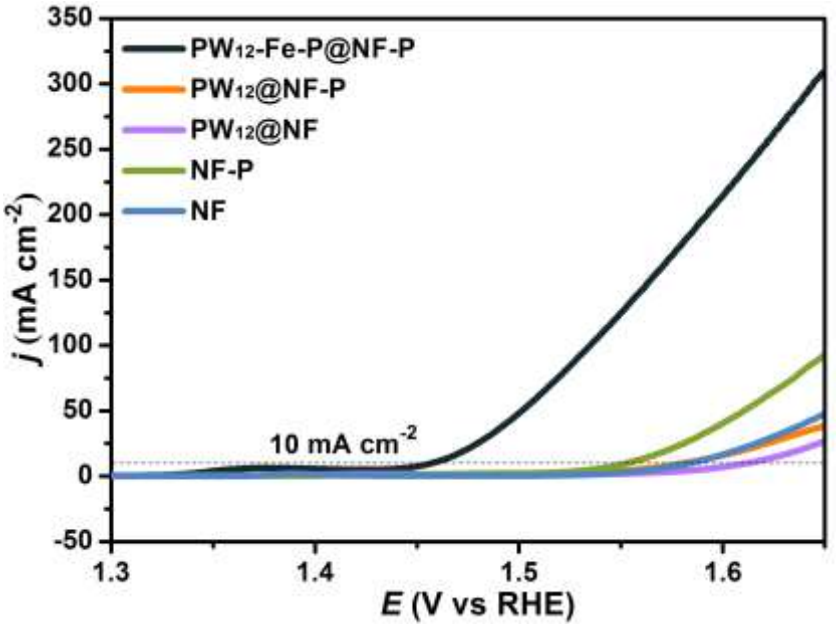

Fig. 13 LSV curves at a scan rate of 1 mV s^{-1} with PW_{12}-Fe-P@NF-P, NF-P and NF in 1.0 M KOH electrolyte, and NF-P and NF in the presence of trace amount of PW_{12} (Abbreviated as PW_{12}@NF-P and PW_{12}@NF) in 1.0 M KOH electrolyte. It should be noted that the Keggin POM will decompose in the strong alkaline aqueous solution.

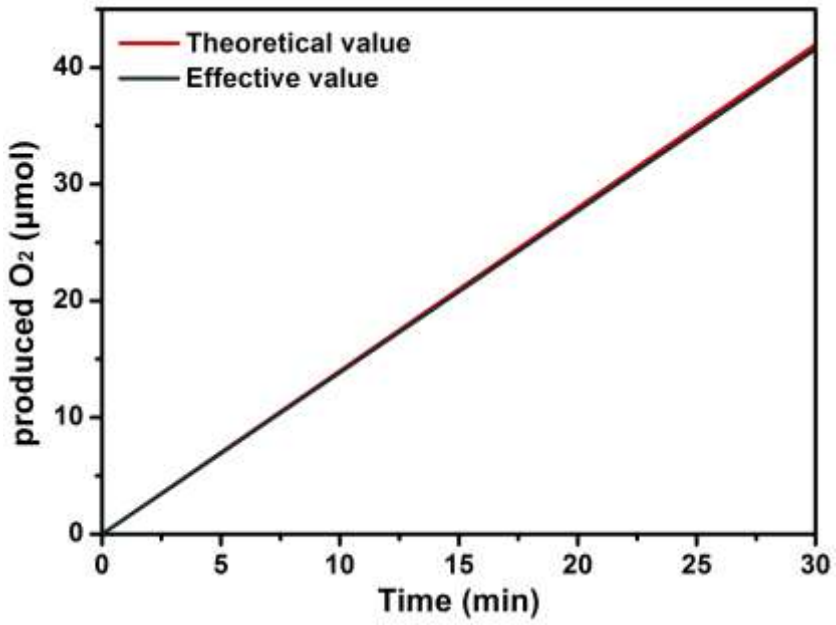

Fig S14. The theoretical and detected amount of O_2 produced by electrocatalytic OER with PW_{12}-Fe-P@NF-P as the catalyst, achieving the Faradic efficiency of ca. 100%.

Table S2. Comparison of OER activity for some reported Fe-electrocatalysts.

Entry	Catalysts	Electrolyte	η at 10 mA cm^{-2} (mV)	References
1	PW_{12}-Fe-P@NF-P	1.0 M KOH	230	The work
2	PMo_{12}-Fe-P@NF-P	1.0 M KOH	247	The work
3	Fe-P@NF-P	1.0 M KOH	252	The work
4	IrO_2@NF-P	1.0 M KOH	275	The work
5	Amorphous FeOOH films	1.0 M Na_2CO_3	550	*J. Am. Chem. Soc., 2014, 136, 2843.*
6	Fe phthalocyanine (FePc)	0.1 M KOH	490	*Appl. Catal., B, 2016, 191, 202.*
7	Fe_3C@NCNTs-NCNFs	1.0 M KOH	284	*J. Mater. Chem. A., 2017, 5, 19672.*
8	Fe_3C/C	1.0 M KOH	382	*Chem. Commun., 2018, 54, 3158.*
9	Fe_3C/PG	1.0 M KOH	299	*Chem. Commun., 2018, 54, 3158.*
10	Fe-based Oxyhydroxides	1.0 M KOH	283	*ACS Energy Let., 2018, 3, 861*
11	$Fe(PO_3)_2$/Ni_2P	1.0 M KOH	177	*PNAS, 2017, 201701562.*
12	$Ni_{0.69}Fe_{0.31}O_x$/C	1.0 M KOH	280	*Langmuir, 2014, 30 (26), 7893*
13	Porous FeNi Oxides Nanosheets	1.0 M KOH	213	*J. Mater. Chem. A., 2016, 4, 14939.*
14	mesoporous NiO/$NiFe_2O_4$ multicomposite hollow nanocages	1.0 M KOH	303	*J. Mater. Chem. A., 2017, 5, 4320.*
15	mesoporous $NiFe_2O_4$ nanorods	1.0 M KOH	342	*Electrochim. Acta, 2016, 211, 871.*
16	$NiFe_2O_4$ nanoparticles	1.0 M KOH	470	*Nanoscale, 2015, 7, 8920.*
17	$NiFe_2O_4$ nanofibers	1.0 M KOH	435	*Nanoscale, 2015, 7, 8920.*
18	mesoporous NiO/$NiFe_2O_4$ biphasic nanorods	1.0 M KOH	302	*Int. J. Hydrogen Energy, 2016, 41, 17976.*
19	NiFe LDH/CNT	1.0 M KOH	300	*J. Am. Chem. Soc., 2013, 135, 8452.*
20	NiFe-LDH nanosheet	1.0 M KOH	300	*Nature Commun., 2014, 5, 4477.*