Electronic Supplementary Information

A general approach to the synthesis of transition metal phosphides nanoarrays on MXene nanosheets for pH-universal hydrogen evolution and alkaline overall water splitting

Liang Yan,‡*[a] Bing Zhang,‡[b] Shangyou Wu,[b] and Jianlin Yu[b]

[a] *School of Chemistry and Materials Engineering, Huizhou University, No. 46 Yanda Road, Huizhou, 516007, China*

[b] *Guangdong Provincial Key Laboratory of Functional Soft Condensed Matter, School of Materials and Energy, Guangdong University of Technology, No. 100 Waihuan Xi Road, Guangzhou Higher Education Mega Center, Guangzhou, 510006, China*

‡ These authors contributed to this work equally.

* Corresponding author. E-mail: yanliang@hzu.edu.cn

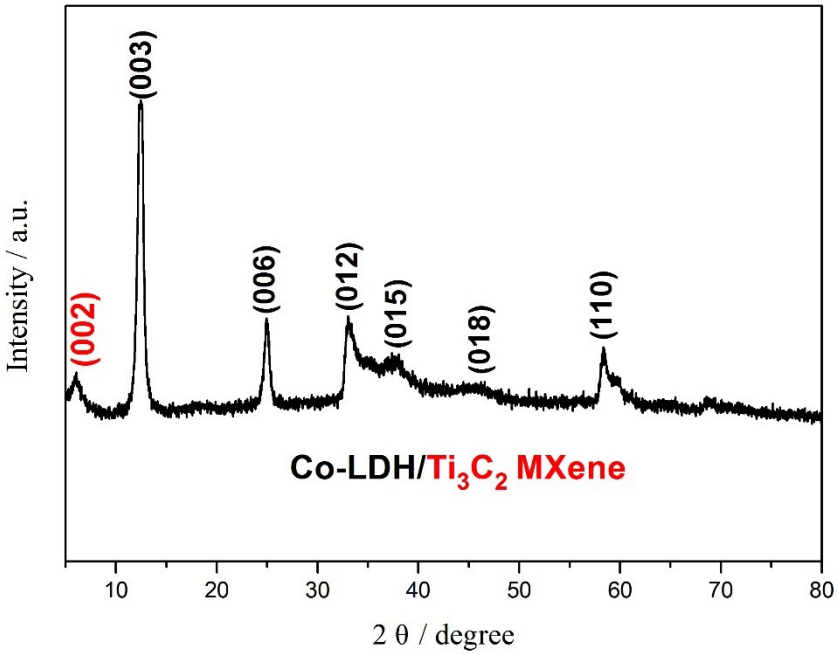

Figure S1. XRD patterns of Co-LDH/Ti_3C_2 MXene.

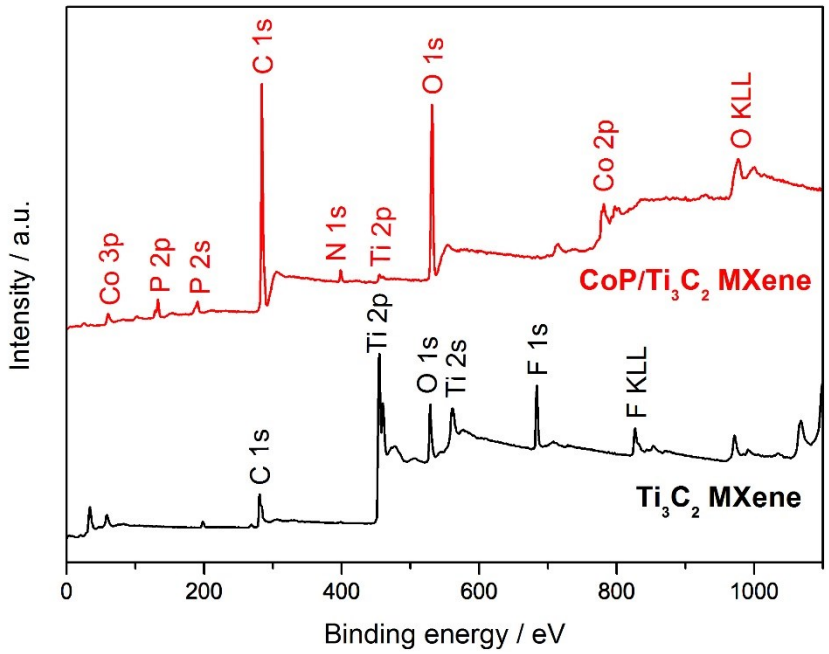

Figure S2. XPS survey spectra of CoP/Ti_3C_2 MXene and Ti_3C_2 MXene.

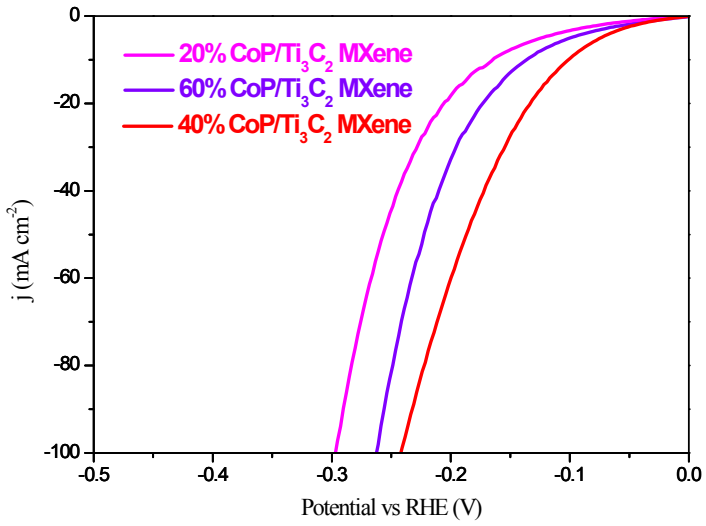

Figure S3. HER polarization curves of CoP/Ti_3C_2 MXene catalysts with varied CoP content measured in 1.0 M KOH.

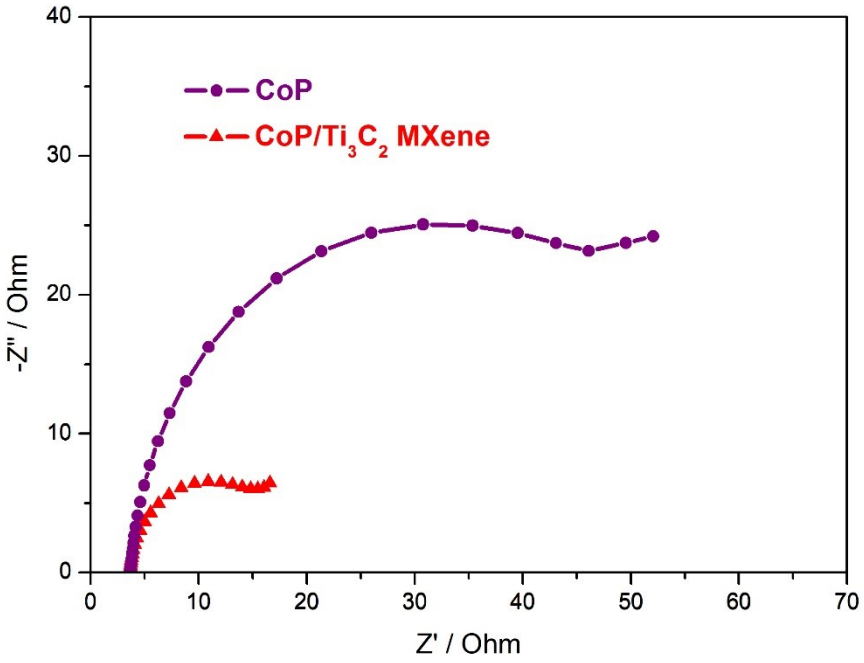

Figure S4. Nyquist plots of the CoP/Ti_3C_2 MXene and MXene-free CoP for HER.

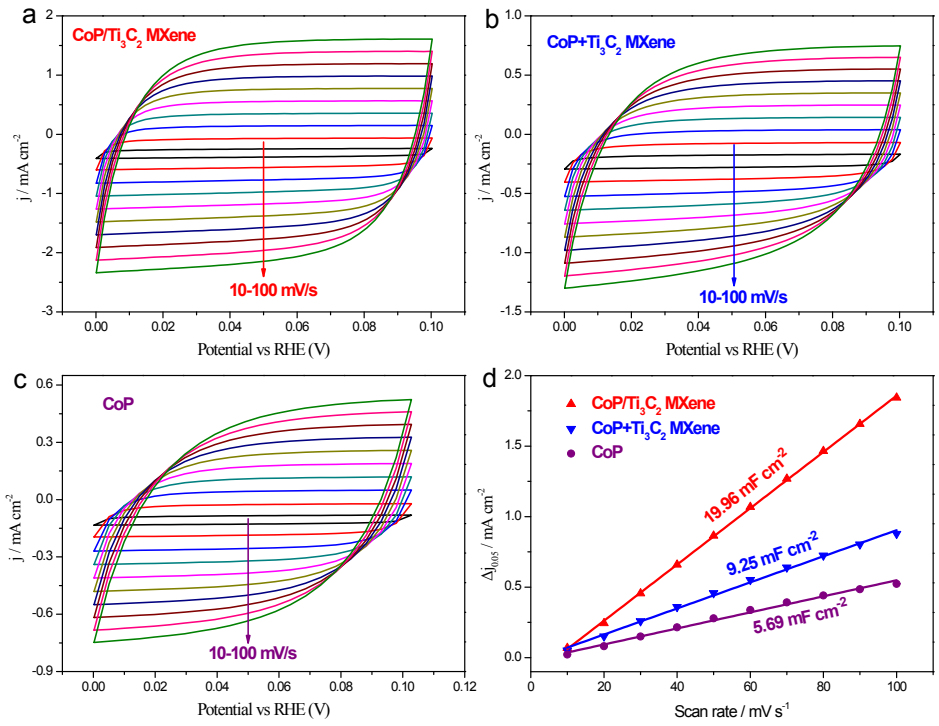

Figure S5. Cyclic voltammograms (CV) curves of (a) CoP/Ti_3C_2 MXene, (b) CoP+Ti_3C_2 MXene, and (c) MXene-free CoP in the region of 0-0.10 V in 1.0 M KOH at various scan rates. (d) Plots of current density differences (Δj) against scan rates of the three catalysts at 0.05 V, where Δj is the difference between anodic and cathodic current densities in CV curves at different scan rates.

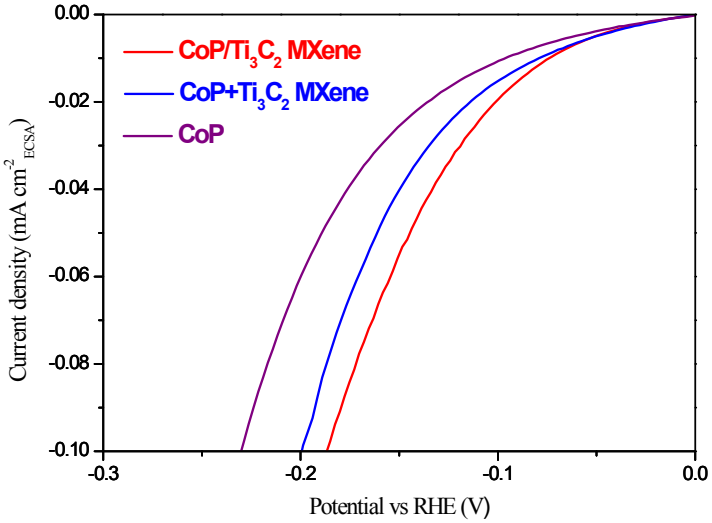

Figure S6. The LSV curves of samples normalized to the ECSA.

The ECSA is acquired from the C_{dl} based on the equation:

$$ECSA = C_{dl}/C_s$$

where C_s is the specific capacitance of the catalyst. From the literature, the specific capacitance was generally found to be in the range of 20-60 μF cm^{-2}, we assumed C_s = 40 μF cm^{-2}.[1]

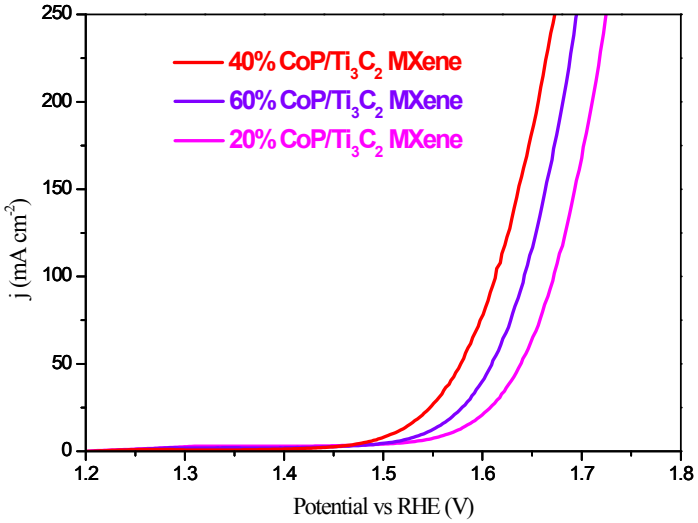

Figure S7. OER polarization curves of CoP/Ti_3C_2 MXene catalysts with varied CoP content measured in 1.0 M KOH.

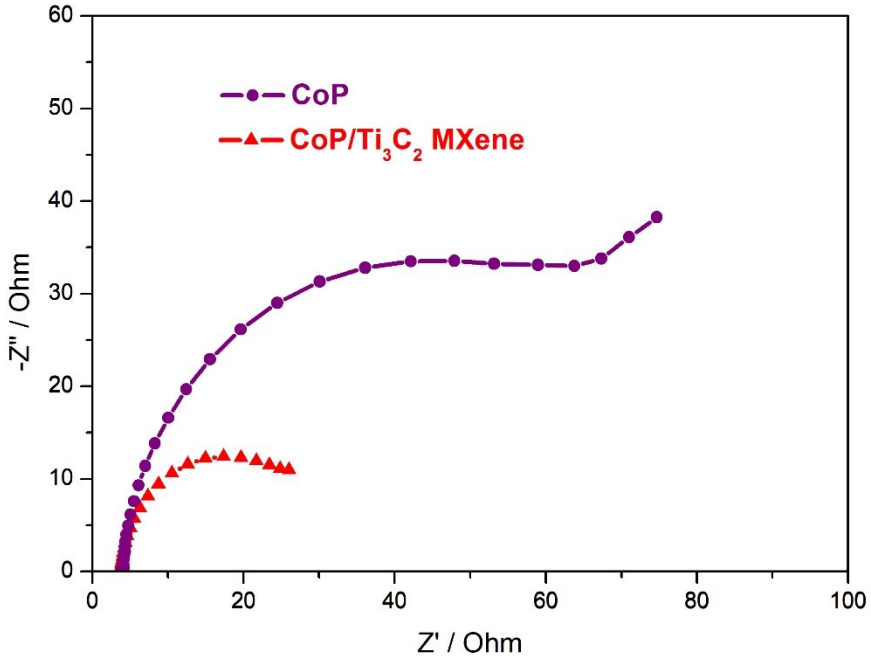

Figure S8. Nyquist plots of the CoP/Ti_3C_2 MXene and MXene-free CoP for OER.

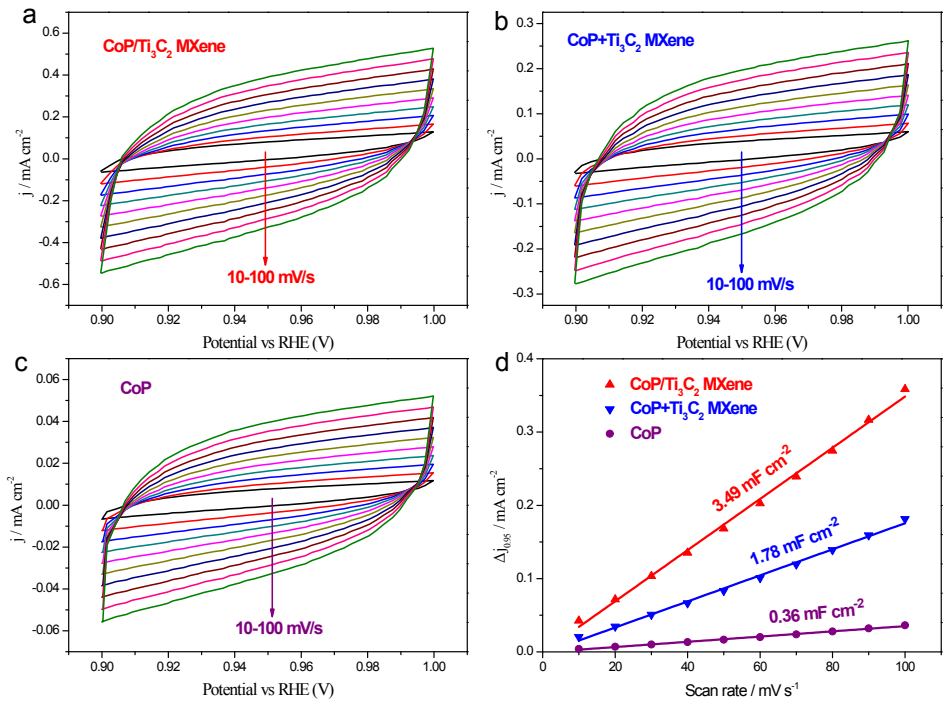

Figure S9. Cyclic voltammograms (CV) curves of (a) CoP/Ti_3C_2 MXene, (b) CoP+Ti_3C_2 MXene, and (c) MXene-free CoP in the region of 0.9-1.0 V in 1.0 M KOH at various scan rates. (d) Plots of current density differences (Δj) against scan rates of the three catalysts at 0.95 V, where Δj is the difference between anodic and cathodic current densities in CV curves at different scan rates.

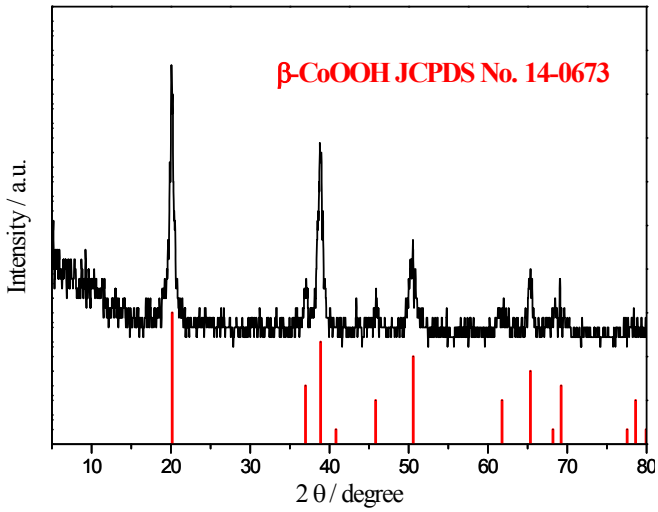

Figure S10. XRD patterns of CoP/Ti_3C_2 MXene after OER test.

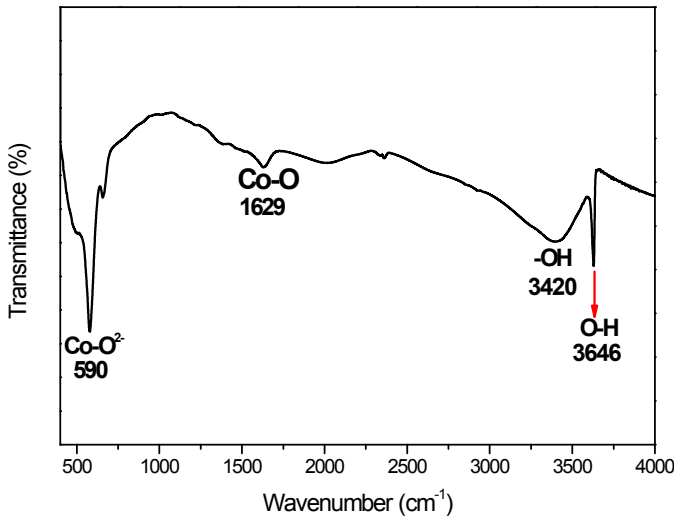

Figure S11. FTIR spectrum of CoP/Ti_3C_2 MXene after OER test.

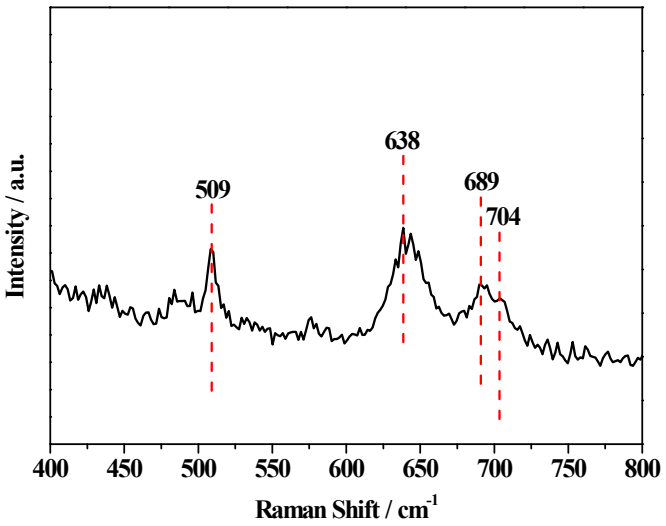

Figure S12. Raman spectra of CoP/Ti_3C_2 MXene after OER test.

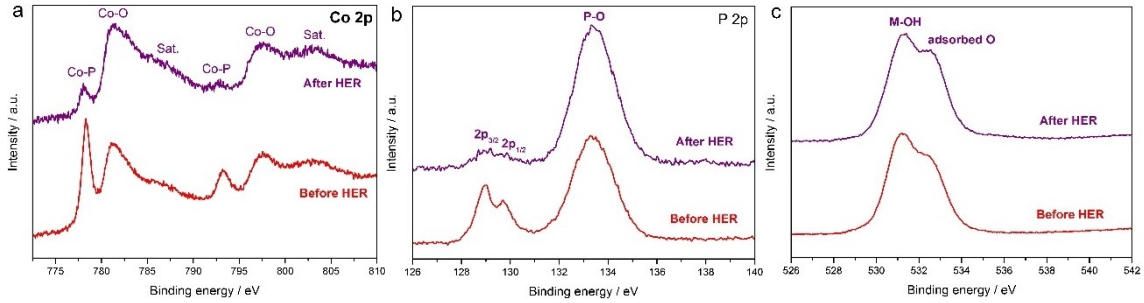

Figure S13. XPS spectra of (a) Co 2p, (b) P 2p, and (c) O 1s of the CoP/Ti_3C_2 MXene before and after HER test in 1.0 M KOH.

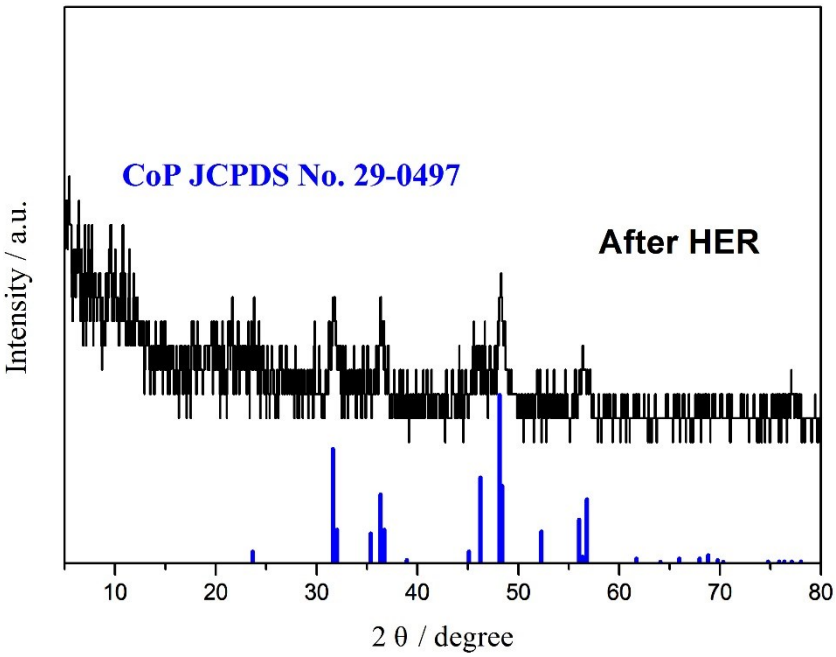

Figure S14. XRD patterns of CoP/Ti_3C_2 MXene after HER test in 1.0 M KOH.

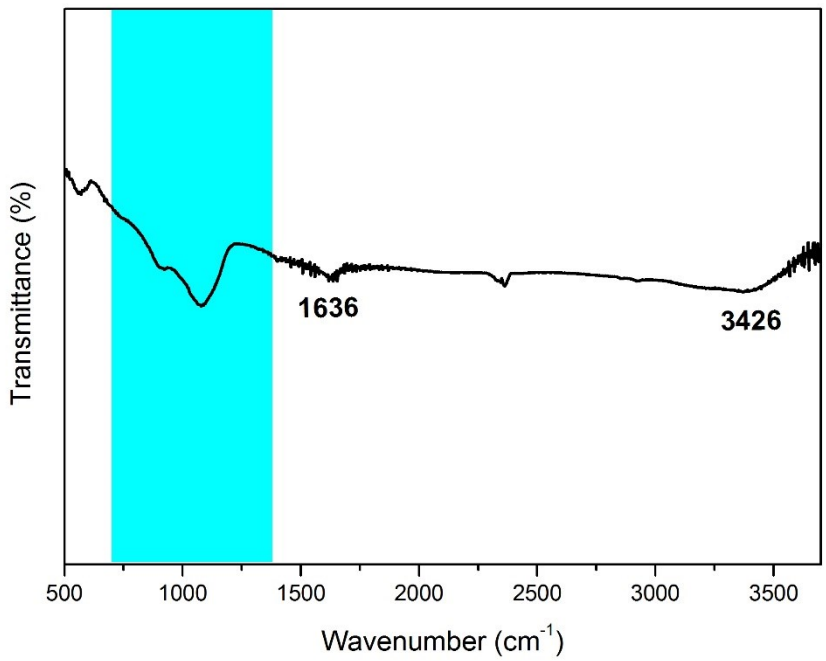

Figure S15. FTIR spectrum of CoP/Ti_3C_2 MXene after HER test in 1.0 M KOH.

The peaks at 1636 and 3426 cm^{-1} originated from the stretching vibration of absorbed water molecules. The bands at 700-1380 cm^{-1} (blue shadows) were associated with the vibration characteristics of Co and P.[2]

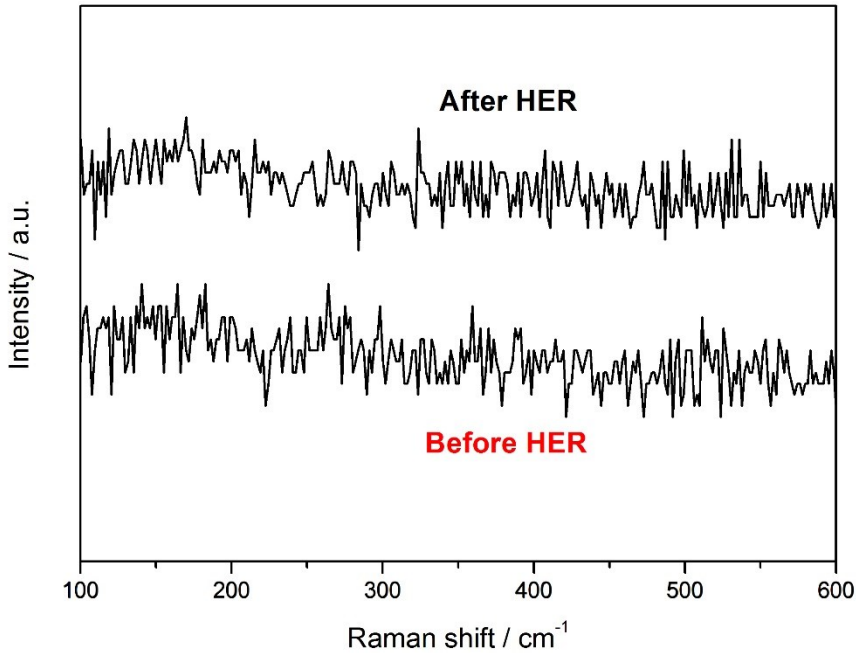

Figure S16. Raman spectrum of CoP/Ti_3C_2 MXene before and after HER test in 1.0 M KOH.

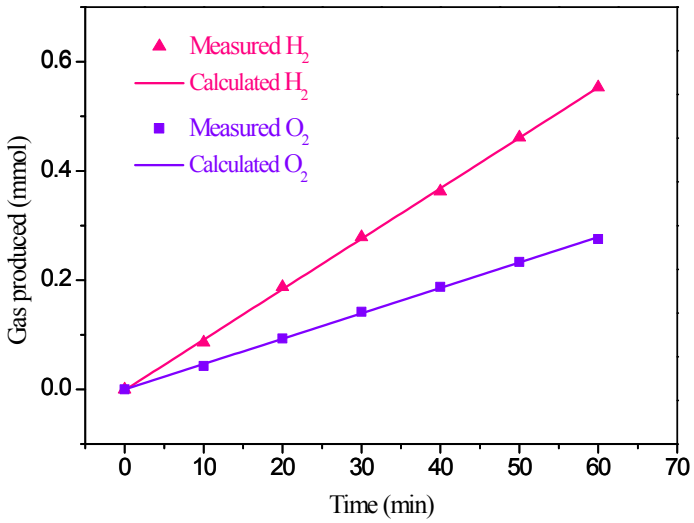

Figure S17. The amount of gas theoretically calculated and experimentally measured versus time for overall water splitting of CoP/Ti_3C_2 MXene.

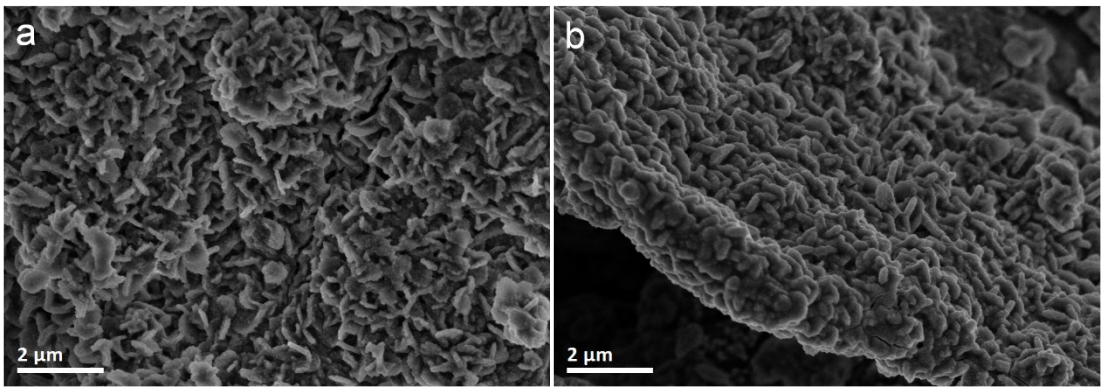

Figure S18. SEM images of CoP/Ti_3C_2 MXene after (a) HER and (b) OER stability test.

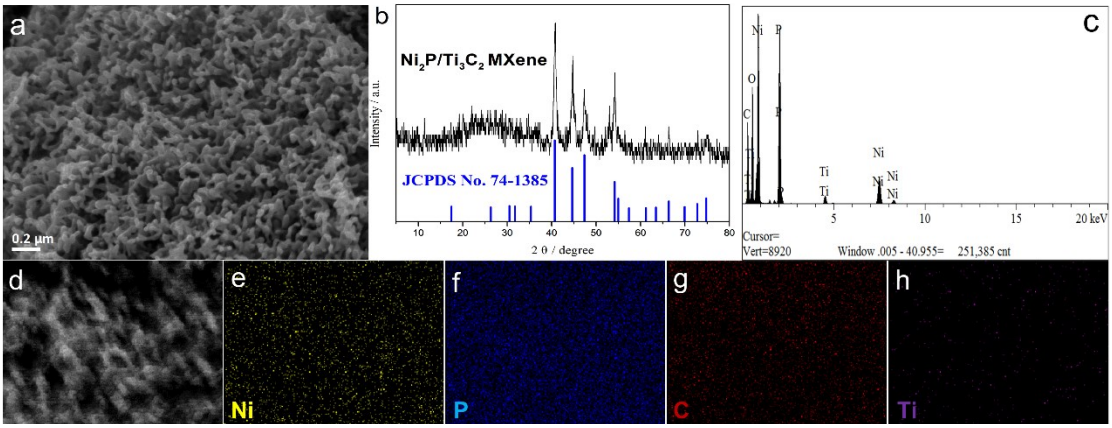

Figure S19. (a) SEM image, (b) XRD patterns, (c) EDX spectrum, and (d-h) Elemental mapping of Ni_2P/Ti_3C_2 MXene.

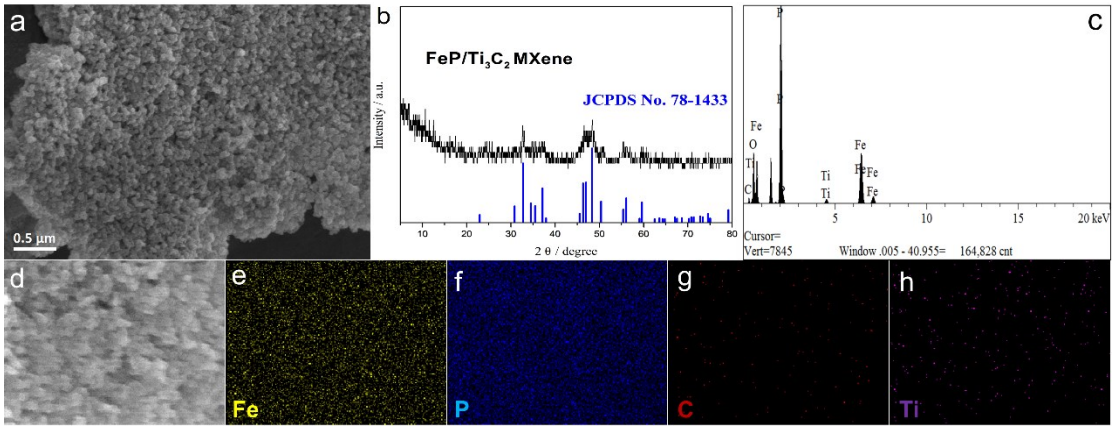

Figure S20. (a) SEM image, (b) XRD patterns, (c) EDX spectrum, and (d-h) Elemental mapping of FeP/Ti_3C_2 MXene.

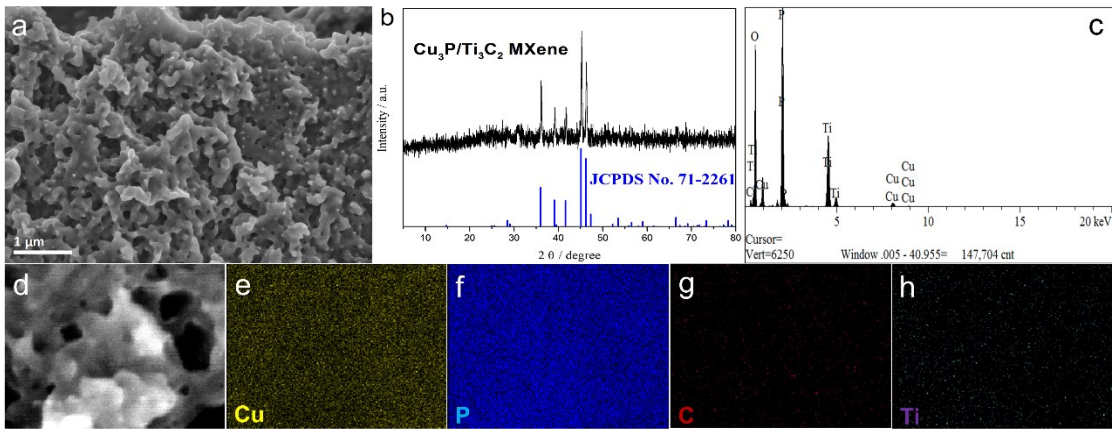

Figure S21. (a) SEM image, (b) XRD patterns, (c) EDX spectrum, and (d-h) Elemental mapping of Cu_3P/Ti_3C_2 MXene.

Table S1. Comparison of HER catalytic performance for non-precious metal electrocatalysts in 1.0 M KOH.

Catalysts	η (mV) at 10 mA cm^{-2}	Tafel slope mV dec^{-1}	References
CoP/CC	209	129	*J. Am. Chem. Soc*. **2014**, *136*, 7587
CoP film	94	42	*Angew. Chem. Int. Ed*. **2015**, *54*, 6251
CoP/NC	154	51	*Chem. Mater*. **2015**, *27*, 7636
CoP NS/C	111	70.9	*Green Chem*. **2016**, *18*, 2287
CoNiP@NF	155	113	*J. Mater. Chem. A* **2016**, *4*, 10195
CoP@NC	129	58	*ACS Catal*. **2017**, *7*, 3824
Co/CoP	193	73.8	*Adv. Energy Mater*. **2017**, *7*, 1602355
CoP@BCN	215	52	*Adv. Energy Mater*. **2017**, *7*, 1601671
CoP/CC	112	74.8	*Chem. Sci*. **2018**, *9*, 1970
CoP/NCNHP	115	66	*J. Am. Chem. Soc*. **2018**, *140*, 2610
NC-CNT/CoP	120	73	*J. Mater. Chem. A* **2018**, *6*, 9009
$Ni_{0.9}Fe_{0.1}PS_3$@MXene	196	NA	*Adv. Energy Mater*. **2018**, *8*, 1801127
CoP_3/CF	100	93.1	*Small* **2019**, *15*, 1904681
CoP/NC	143	91	*Adv. Funct. Mater*. **2019**, *29*, 1807976
CoP/CC	88	66	*ACS Catal*. **2019**, *9*, 3744
CoP/NPC/TF	80	50	*Adv. Energy Mater*. **2019**, *9*, 1803970
CoP/CF	75	65	*Angew. Chem. Int. Ed*. **2019**, *58*, 4679
$Co_{0.31}Mo_{1.69}C$/MXene/NC	75	43	*Adv. Energy Mater*. **2019**, *9*, 1901333
Ru_{SA}-N-S-$Ti_3C_2T_x$	99	NA	*Adv. Mater*. **2019**, *31*, 1903841
NiFe-LDH/MXene/NF	132	70	*Nano Energy* **2019**, *63,* 103880
$MoSe_2/Ti_3C_2T_x$	95	91	*Electrochim. Acta* **2019**, *326*, 134976
Co-MoS_2/Mo_2CT_x	112	82	*Nanoscale* **2019**, *11*, 10992
CoP/CC	122	83.3	*Adv. Funct. Mater*. **2020**, *30*, 1909618
CoP@rGO	170	61.72	*Appl. Catal. B Environ*. **2020**, *265,*118576
CoP NFs	136	56.2	*ACS Catal*. **2020**, *10*, 412
CoP@NF	155	96.98	*Nano Energy* **2020**, *67,* 104174
CoP/CC	87	72	*Appl. Catal. B Environ*. **2020**, *253, 21*
CoP/PC	76	NA	*Small* **2020**, *16*, 1900550
$Mo_2C/Ti_3C_2T_x$@NC	75	59.2	*J. Mater. Chem. A* **2020**, *8*, 7109
CoP/Ti_3C_2 MXene	102	68.7	This work

NA: Not available

Table S2. Comparison of HER catalytic performance for non-precious metal electrocatalysts in 0.5 M H_2SO_4.

Catalysts	η (mV) at 10 mA cm^{-2}	Tafel slope mV dec^{-1}	References
CoP/CC	67	51	*J. Am. Chem. Soc*. **2014**, *136*, 7587
CoP/CNT	122	54	*Angew. Chem. Int. Ed*. **2014**, *53*, 6710
CoP/Ti	~75	50	*Angew. Chem. Int. Ed*. **2014**, *53*, 5427
Co_2P NPs	95	45	*Chem. Mater.* **2015**, *27,* 3769
CoNiP@NF	60	39	*J. Mater. Chem. A* **2016**, *4*, 10195
Mo_2CT_x MXene	283	NA	*ACS Energy Lett*. **2016**, *1*, 589
CoP@BCN-1	87	46	*Adv. Energy Mater*. **2017**, *7*, 1601671
MoS_2/Ti_3C_2-MXene@C	135	45	*Adv. Mater.* **2017**, *29*, 1607017
CoP/NCNHP	140	53	*J. Am. Chem. Soc*. **2018**, *140*, 2610
PANI/CoP HNWs-CFs	57	34.5	*J. Am. Chem. Soc*. **2018**, *140*, 5118
IE-MoS_2-Ti_3C_2@240	110	40	*J. Mater. Chem. A*, **2018**, *6*, 16882
Ti_2CT_x nanosheets	75	100	*Nano Energy* **2018***, 47,* 512
CoP/NC	116	103	*Adv. Funct. Mater.* **2019**, *29*, 1807976
CoP_3/CF	125.3	50.5	*Small* **2019**, *15*, 1904681
CoP@PC-750	72	49	*Small* **2019**, *15*, 1900550
CoP/NPC/TF	91	54	*Adv. Energy Mater.* **2019**, *9*, 1803970
CoP/CC	78	61	*ACS Catal*. **2019**, *9*, 3744
CoP/CF	65	57	*Angew. Chem. Int. Ed*. **2019**, *58*, 4679
$Co_{0.31}Mo_{1.69}C$/MXene	81	24	*Adv. Energy Mater.* **2019**, *9*, 1901333
Ru_{SA}-N-S-$Ti_3C_2T_x$	76	90	*Adv. Mater.* **2019**, *31*, 1903841
CoP_2/CC	125	73	*Sci. Adv.* **2020**, *6*, eaaw8113
CoP NFs	122	54.8	*ACS Catal.* **2020**, *10*, 412
CoP/CNT	85	63	*Angew. Chem. Int. Ed.* **2020**, *59*, 4154
CoP/CC	79	61	*Appl. Catal. B Environ.* **2020***, 253, 21*
$Mo_2C/Ti_3C_2T_x$@NC	75	59.2	*J. Mater. Chem. A* **2020**, *8*, 7109
CoP/Ti_3C_2 MXene	71	57.6	This work

Table S3. Comparison of HER catalytic performance for non-precious metal electrocatalysts in 1.0 M PBS.

Catalysts	η (mV) at 10 mA cm^{-2}	Tafel slope mV dec^{-1}	References
CoP/CC	106	93	*J. Am. Chem. Soc.* **2014**, *136*, 7587
CoP/Ti	149	111	*Chem. Mater*. **2014**, *26*, 4326
$CoNi_4P_2$	430	NA	*Energy Environ. Sci*. **2014**, *7*, 329
CoP-MNA/NF	~180[a]	189	*Adv. Funct. Mater.* **2015**, *25*, 7337
NiCoP/rGO	124	91	*Adv. Funct. Mater.* **2016**, *26*, 6785
CoP NW/Hb	121	106	*Nano Research* **2017**, *10*, 1010
CoP@BCN-1	122	59	*Adv. Energy Mater.* **2017**, *7*, 1601671
Ni_2P@NPCNFs	185.3	230.3	*Angew. Chem. Int. Ed.* **2018**, *57*, 1963
$Ni_{0.1}Co_{0.9}P$/CFP	125	103	*Angew. Chem. Int. Ed*. **2018**, *57*, 15445
CoP@NPMG	126	62	*Nanoscale* **2018**, *10*, 2603
V-CoP/CC	123	72.6	*Chem. Sci.* **2018**, 9, 1970
CoP/NiCoP/NC	123	78	*Adv. Funct. Mater.* **2019**, *29*, 1807976
CoP_3/CF	136	121.7	*Small* **2019**, *15*, 1904681
CoP/CC	130	94	*ACS Catal*. **2019**, *9*, 3744
CoP/CF	97	89	*Angew. Chem. Int. Ed*. **2019**, *58*, 4679
$Co_{0.31}Mo_{1.69}C$/MXene	126[b]	46	*Adv. Energy Mater.* **2019**, *9*, 1901333
Ru_{SA}-N-S-$Ti_3C_2T_x$	275[c]	NA	*Adv. Mater.* **2019**, *31*, 1903841
Co_2P/NC-900	315	166	*ChemSusChem* **2020**, *13*, 351
CoP/CC	136	117	*Appl. Catal. B Environ.* **2020**, *253, 21*
B-CoP/CNT	79	80	*Angew. Chem. Int. Ed.* **2020**, *59*, 4154
$Mo_2C/Ti_3C_2T_x$@NC	114[b]	80.3	*J. Mater. Chem. A* **2020**, *8*, 7109
CoP/Ti_3C_2 MXene	124	96.8	This work

[a]: 0.5 M PBS; [b]: 0.1 M PBS; [c]: 0.5 M Na_2SO_4.

Table S4. Comparison of OER catalytic performance for non-precious electrocatalysts in 1.0 M KOH.

Catalysts	η (mV) at 10 mA cm^{-2}	Tafel slope mV dec^{-1}	References
CoP-MNA/NF	290	65	*Adv. Funct. Mater.* **2015**, *25*, 7337
Co-P film	345	47	*Angew. Chem. Int. Ed.* **2015**, *54*, 6251
CoP NR/C	320	71	*ACS Catal.* **2015**, *5*, 6874
NiCoP/NF	280	87	*Nano Lett.* **2016**, *16*, 7718
CoMnP nanoparticles	330	61	*J. Am. Chem. Soc.* **2016**, *138*, 4006
CoP/rGO	340	66	*Chem. Sci.* **2016**, *7*, 1690
CoP NS/C	277	85.6	*Green Chem.* **2016**, *18*, 2287
g-C_3N_4/Ti_3C_2 MXene	340	NA	*Angew. Chem. Int. Ed*. **2016**, *55*, 1138
CoBDC/$Ti_3C_2T_x$	410[a]	48.2	*ACS Nano* **2017**, *11*, 5800
NiCoP/Ti	310	52	*Adv. Mater. Interfaces* **2016**, *3*, 1500454
NiCoP/C	330	96	*Angew. Chem. Int. Ed.* **2017**, *56*, 3897
FeNi-LDH/Ti_3C_2-MXene	298	43	*Nano Energy* **2018**, *44*, 181
$Ni_{0.7}Fe_{0.3}PS_3$@MXene	282	36.5	*Adv. Energy Mater.* **2018**, *8*, 1801127
NiCoS/$Ti_3C_2T_x$	365	58.2	*ACS Appl. Mater. Interfaces* **2018**, *10*, 22311
CoP/NCNHP	310	70	*J. Am. Chem. Soc.* **2018**, *140*, 2610
S:Co_2P@CC	290	82	*Chem. Mater.* **2018**, *30*, 8861
CoP@NPMG	276	54	*Nanoscale* **2018**, *10*, 2603
CoP@PC-750	283	53	*Small* **2019**, *15*, 1900550
CoP/CoO	295	73	*Nano Energy* **2019**, *56,* 109
NiFe-LDH/MXene/NF	229	44	*Nano Energy* **2019**, *63,* 103880
CoP/TiO_x	337	72.1	*Small* **2020**, *16*, 1905075
Co_2P NRs	372.2	111.8	*J. Am. Chem. Soc.* **2020**, *142*, 8490
CoP/CC	340	87	*Adv. Funct. Mater.* **2020**, *30*, 1909618
CoP NFs	323	49.6	*ACS Catal.* **2020**, *10*, 412
CoP/Ti_3C_2 MXene	280	95.4	This work

[a]: 0.1 M KOH

Table S5. Summary of recent reported representative of bifunctional non-noble metal based catalysts for overall water-splitting in 1.0 M KOH.

Catalysts	Potential (V) at 10 mA cm^{-2}	References
Co-P film	1.65	*Angew. Chem. Int. Ed.* **2015**, *54*, 6251
CoP-MNA	1.62	*Adv. Funct. Mater.* **2015**, *25*, 7337
CoP NR	1.587	*ACS Catal.* **2015**, *5*, 6874
NiCoP/Ti	1.64	*Adv. Mater. Interfaces* **2016**, *3*, 1500454
CoP nanosheets	1.54	*Green Chem.* **2016**, *18*, 2287
CoP/GO	1.7	*Chem. Sci.* **2016**, *7*, 1690
CoP/CC	1.61	*ChemSusChem* **2016**, *9*, 472
Fe-CoP/Ti	1.60	*Adv. Mater.* **2017**, *29*, 1602441
CoP NA/CC	1.65	*ChemElectroChem* **2017**, *4*, 1840
Ni-Co-P HNBs	1.62	*Energy Environ. Sci.* **2018**, *11*, 872
S:CoP@NF	1.617	*Nano Energy* **2018**, *53*, 286
CoP-400	1.65	*Adv. Energy Mater.* **2018**, *8*, 1802445
CoP@a-CoO_x plate	1.66	*Adv. Sci.* **2018**, *5*, 1800514
CoP/NCNHP	1.64	*J. Am. Chem. Soc.* **2018**, *140*, 2610
NC-CNT/CoP	1.63	*J. Mater. Chem. A* **2018**, *6*, 9009
CoP@NPMG	1.58	*Nanoscale* **2018**, *10*, 2603
$Ni_{0.7}Fe_{0.3}PS_3$@MXene || $Ni_{0.9}Fe_{0.1}PS_3$@MXene	1.65	*Adv. Energy Mater.* **2018**, *8*, 1801127
NiFe-LDH/MXene/NF	1.51	*Nano Energy* **2019**, *63,* 103880
Er-CoP/CC	1.58	*J. Mater. Chem. A* **2019**, *7*, 5769
CoP@NiFe-OH/SPNF	1.53	*Nano Energy* **2019**, *63*, 103821
CoP@PC-750	1.60	*Small* **2020**, *16*, 1900550
CoP NFs	1.65	*ACS Catal*. **2020**, *10*, 412
O-CoP	1.60	*Adv. Funct. Mater.* **2020**, *30*, 1905252
CoP/Ti_3C_2 MXene	1.578	This work

Reference

1 C. C. L. McCrory, S. Jung, J. C. Peters and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2013, **135**, 16977-16987.

2 N. Ismail, M. Madian and A. A. El-Meligi, *J. Alloys Compd.*, 2014, **588**, 573-577.