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Electronic Supplementary Information

MXene Supported Co_xA_y (A = OH, P, Se) Electrocatalysts for Overall Water Splitting: Unveiling the Role of Anions on Intrinsic Activity and Stability

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Standartd practices followed in the experimental evaluation of electrocatalytic activity:

The electrocatalytic performance of the as-prepared catalysts was examined by using a standard three-electrode system in 1 mol L^{-1} KOH solution (free from impurities).

1. LSV Measurements:

The given LSV data for every sample were measured after running 10 consecutive CV cycles (0.9 to 1.7 V vs RHE at the scane rate of 5 mV sec^{-1}).

2. Overpotenial:

Three duplicate electrodes were prepared for every sample and meansured the LSV to calculate the overpotentails with error analysis. The overpotential at 10 mA cm^{-2} current density with iR compensation for different catalysts showed less than 5% error. Thus, the given overpotential with error analysis manifest the intrinsic performance of the electrocatalysts.

3. Mass Normalized Activity:

The geometrical area normalized current density (mA cm^{-2}) reflects the area of electrodes only. Hence, we reported the geometrical area normalized activity along with mass normalized activity(A g^{-1}).

4. Electrochemically Active Surface Area (ECSA) Normalized Activity:

The ECSA, a key descriptor, influencing the electrocatalytic reactions. Thus, the CV method was used to calculate the ECSA. The double-layer capacitance of the electrodes in a non-Faradaic potential region (0.1 V window about OCP) was identified from CV graph. Then, the follwing formula was used to caluculate ECSA.

ECSA = C_{dl} / Cs, taking Cs (specific capacitance) to equal 0.040 mF cm^{-2}, as adopted from a previous study on Co-based OER catalysts.

Later, the current density (10 mA cm^{-2}) of each sample was normalized with its ECSA.

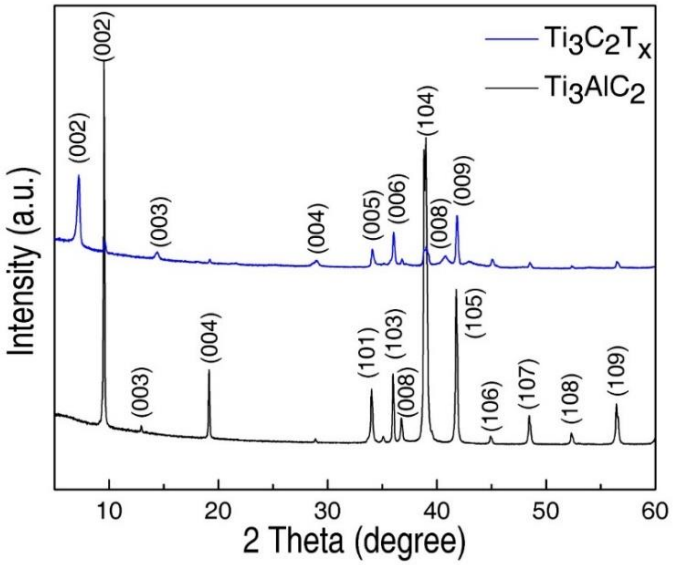


Fig. S1. XRD pattern of the Ti_3AlC_2 phase and the $Ti_3C_2T_x$ MXene phase.

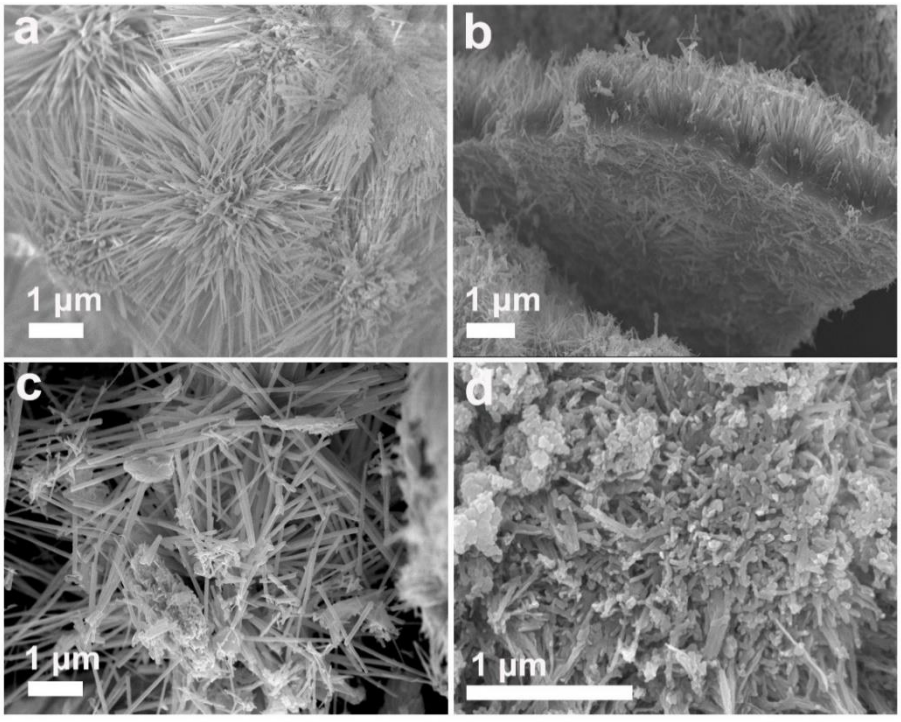


Fig. S2. (a) SEM image of bare Co(OH)F, (b) Co(OH)F/MXene precursor, (c) bare CoP, and (d) bare Co_7Se_8.

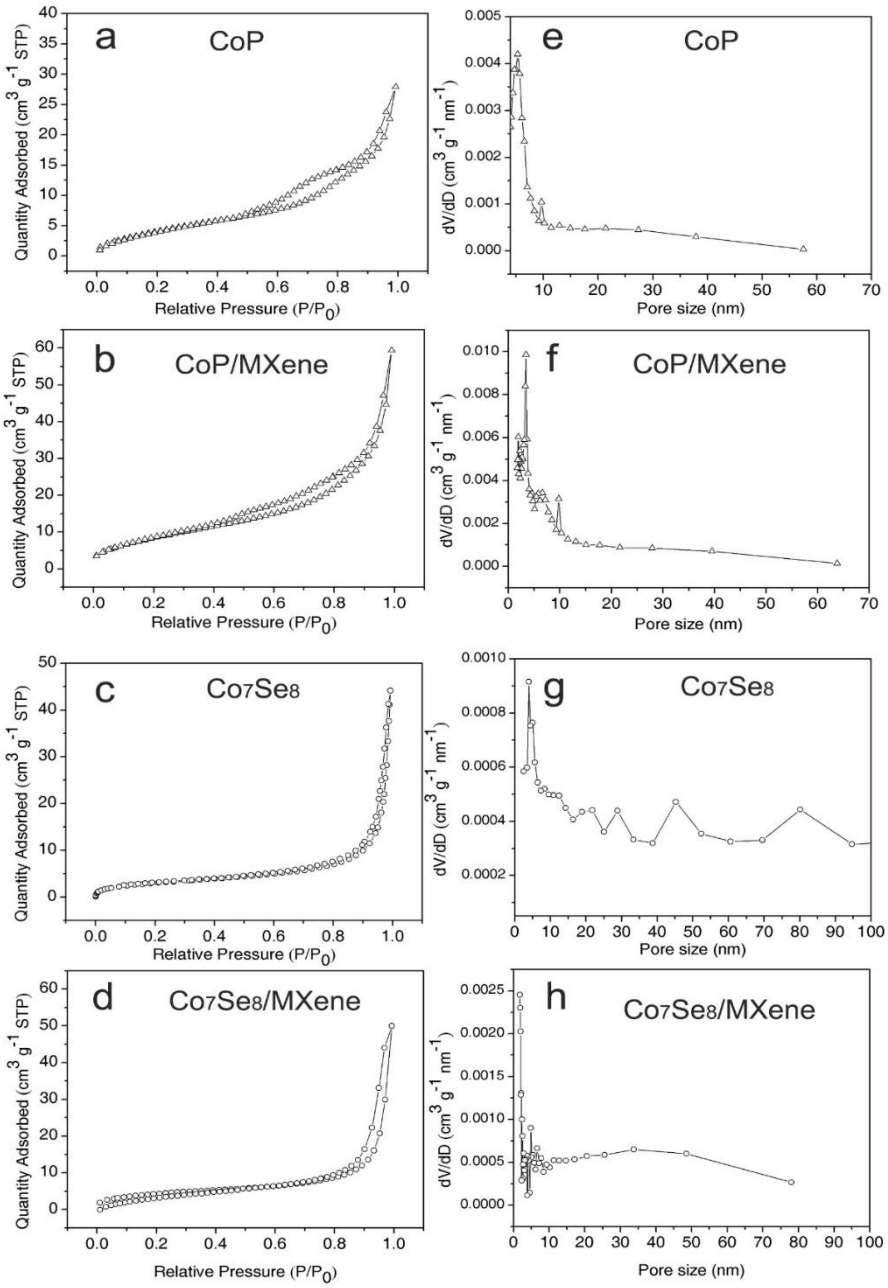


Fig. S3. (a-d) N_2 adsorption-desorption isotherm of various catalysts; (e-h) corresponding pore size distribution curves.

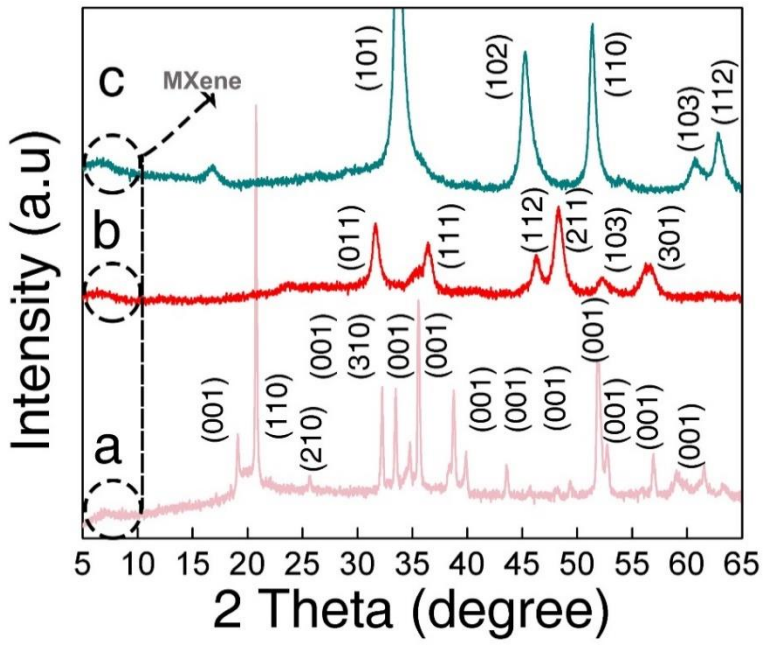


Fig. S4. (a) XRD pattern of Co(OH)F/Mxene, (b) CoP/Mxene, and (c) Co_7Se_8/MXene.

XRD analysis of the precursor Co(OH)F/MXene confirmed the formation of an orthorhombic crystalline phase of Co(OH)F (matching JCPDS card no. 50-0827) [**J. Mater. Chem. A, 2013, 1, 7511**]. The CoP/MXene showing diffraction peaks at 2θ of 31.6, 36.4, 46.3, 48.3, 52.2, and 56.2°, respectively corresponding to the (011), (111), (112), (211), (103), and (301) planes of CoP (JCPDS no. 29-0497) [**J. Am. Chem. Soc. 2018, 140, 5241**]. The Co_7Se_8/Mxene exhibited peaks at 33.5°, 45.0°, 51.2°, 60.8°, 62.8°, and 70.7° are respectively assigned to the crystal planes of (101), (102), (110), (103), (112), and (202) of the hexagonal structure of $Co_{0.85}Se$ (JCPDS No. 52-1008) [**ACS Appl. Mater. Interfaces 2017, 9, 30703**]. Furthermore, all of the samples showed a hump at 2θ of ~7-8.0°, which could be ascribed to the concurrent presence of MXene.

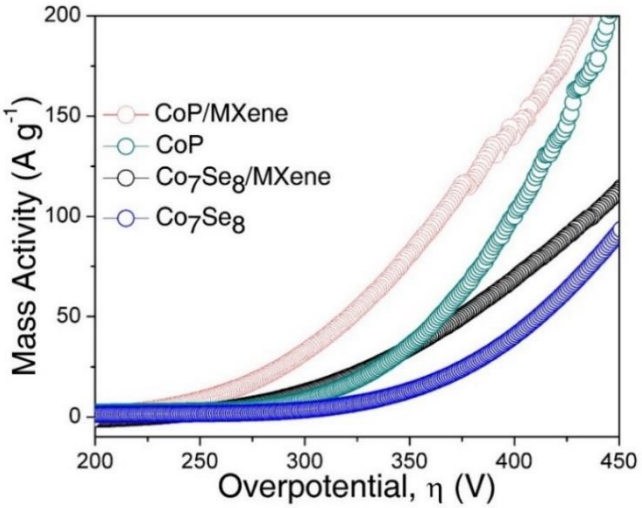


Fig. S5. Mass activity graph for various catalysts.

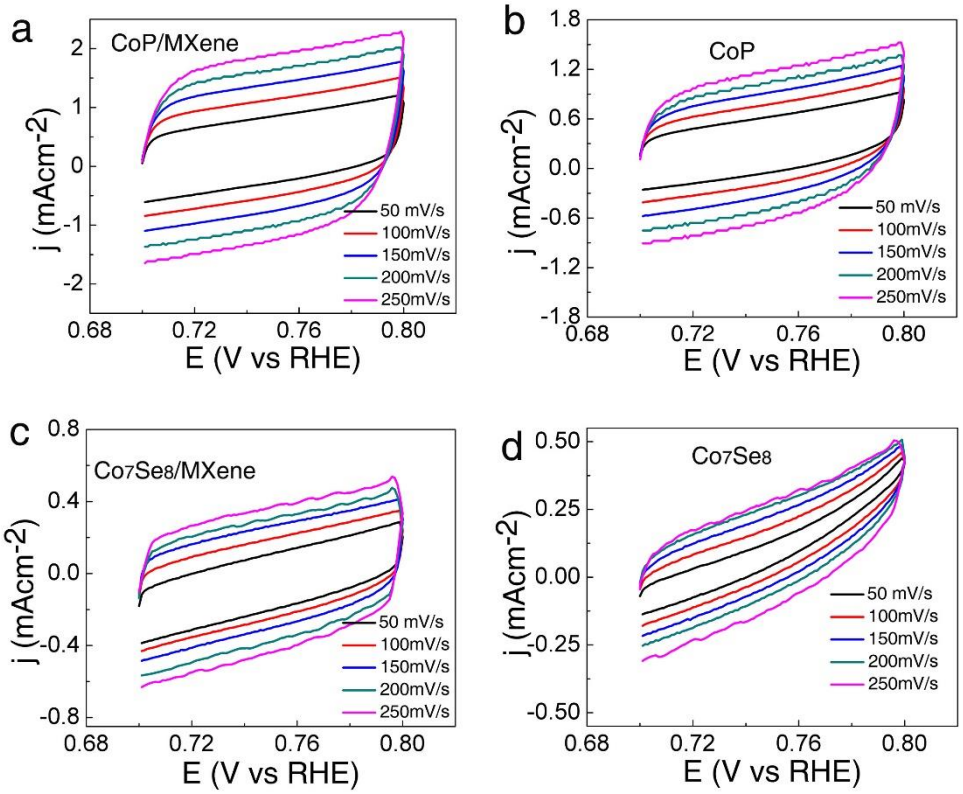


Fig. S6. Cyclic voltammograms measured in non-Faradaic region of the voltammogram at different scan rate for different catalysts in 1 M KOH. The observed current is due to capacitive charging.

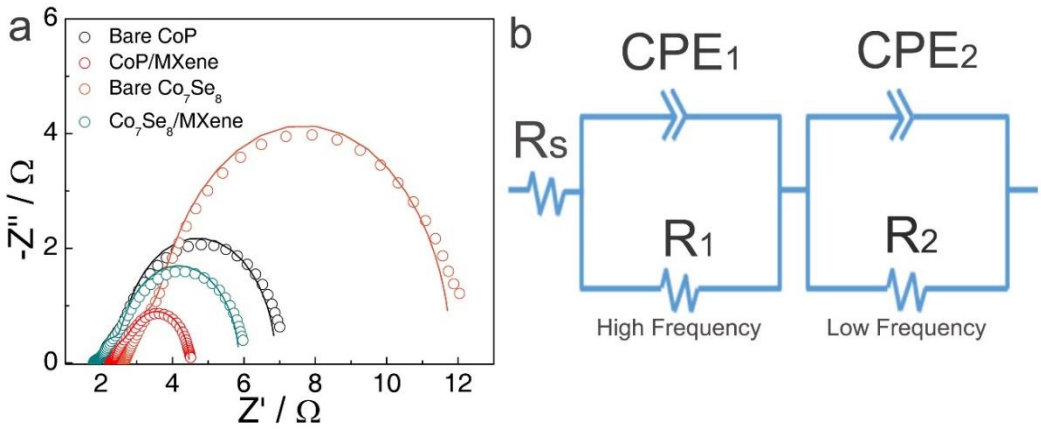
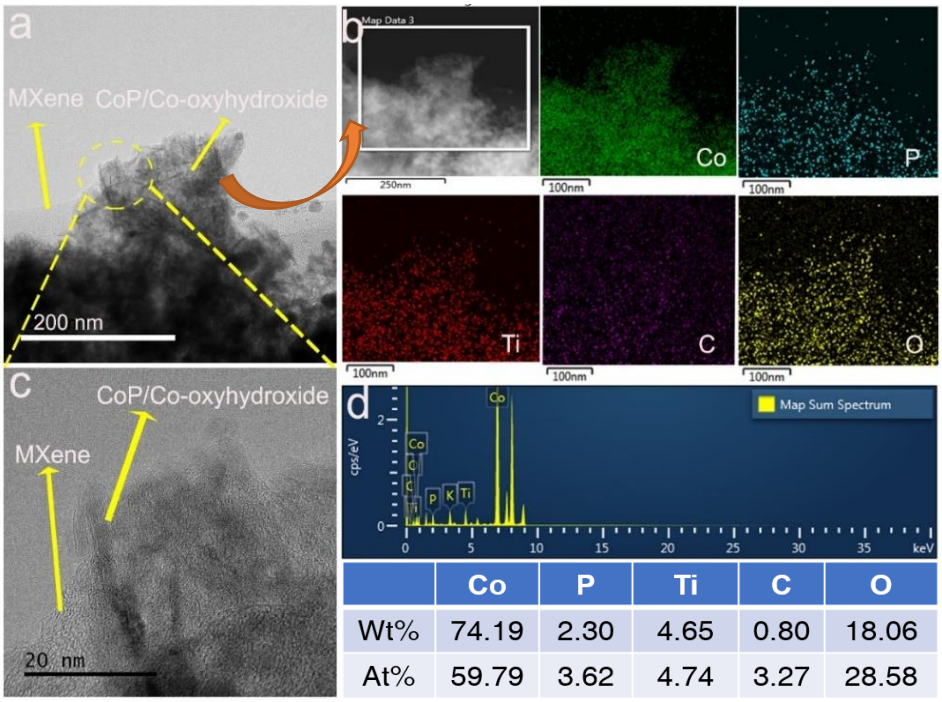
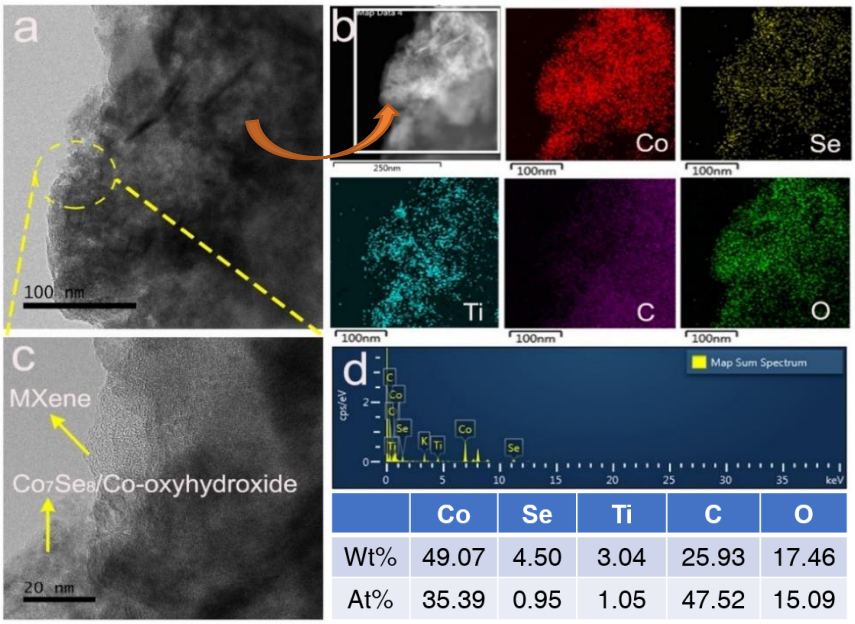


Fig. S7. (a) Nyquist plots for various catalysts (measured at 1.63 V vs RHE) in the frequency range from 0.1 Hz to 100 KHz (Symbol: raw data and Line: fitted data), and (b) The two-time constant serial (2TS) model used for fitting the impedance spectra of the catalysts.R_s is internal solution resistance, R_1(higher frequency) is related to resistance of the electrolyte filling the pores of the electrode, and R_2(lower frequency) is reflecting the charge transfer kinetics of the electrode during OER catalysis.Refere Table S3 for impedance parameters.



	Co	P	Ti	C	O
Wt%	74.19	2.30	4.65	0.80	18.06
At%	59.79	3.62	4.74	3.27	28.58

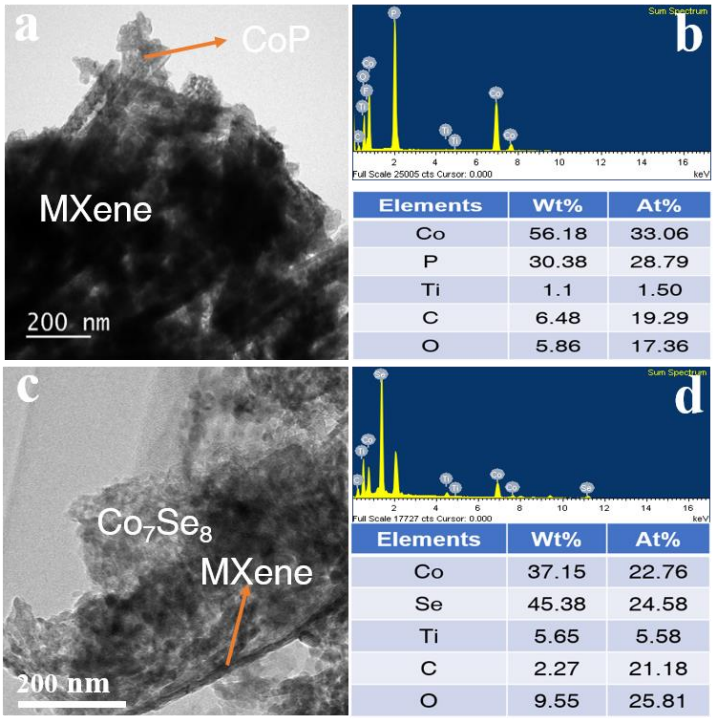
Fig. S8. (a) TEM image of CoP/MXene (Post-OER sample), (b) HAADF-TEM image and corresponding elemental mapping, (c) high resolution TEM image of CoP/MXene (Post-OER sample), and (d) EDX pattern with elemental composition of CoP/MXene (Post-OER sample).



	Co	Se	Ti	C	O
Wt%	49.07	4.50	3.04	25.93	17.46
At%	35.39	0.95	1.05	47.52	15.09

Fig. S9. (a) TEM image of Co_7Se_8/MXene (Post-OER sample), (b) HAADF-TEM image and corresponding elemental mapping, (c) high resolution TEM image of Co_7Se_8/MXene (Post-OER sample), and (d) EDX pattern with elemental composition of Co_7Se_8/MXene (Post-OER sample).

Note: The EDX peak of Potassium is due to the adsorption of alkaline electrolyte (KOH) on the surface of the catalyst during OER catalysis. The unlabelled peaks are due to copper grid.



Elements	Wt%	At%
Co	56.18	33.06
P	30.38	28.79
Ti	1.1	1.50
C	6.48	19.29
O	5.86	17.36

Elements	Wt%	At%
Co	37.15	22.76
Se	45.38	24.58
Ti	5.65	5.58
C	2.27	21.18
O	9.55	25.81

Fig. S10. (a) TEM image of CoP/MXene (Fresh sample), and (b) corresponding EDS spectrum with elemental composition. (c) TEM image of Co_7Se_8/MXene (Fresh sample), and (d) corresponding EDX spectrum with elemental composition.

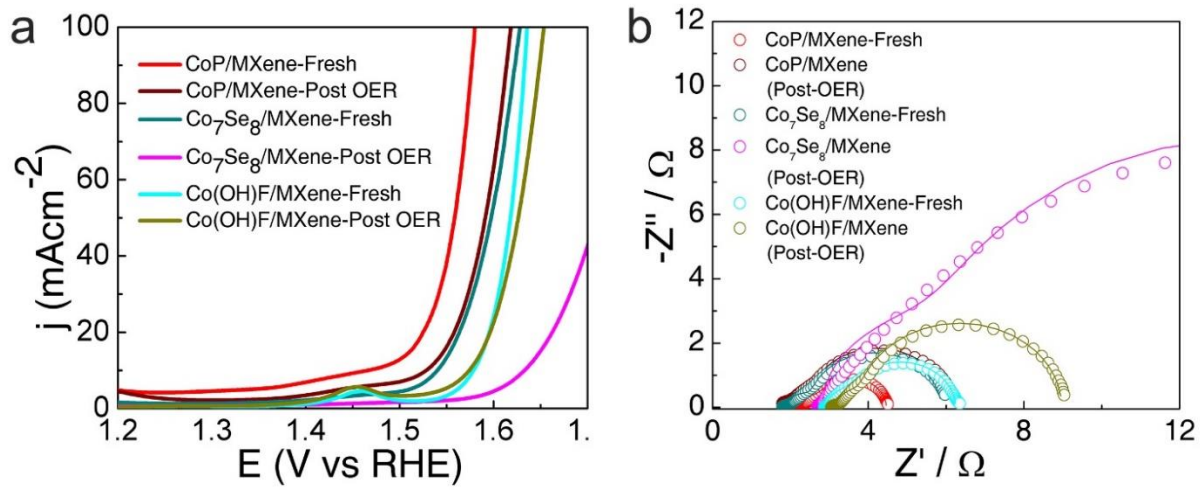


Fig. S11. Comparison between CoP/MXene, Co_7Se_8/MXene and Co(OH)F/MXene catalysts after OER catalysis for 10 h. (a) OER polarization curves (iR-compensated) for various catalysts in 1 mol L^{-1} KOH. (b) Nyquist plots for various catalysts (measured at 1.63 V vs RHE) in the frequency range from 0.1 Hz to 100 KHz. 2TS model was used for fitting the impedance spectra of the catalysts (Symbol: raw data and Line: fitted data). Refere Table S6 for impedance parameters.

Note: Conductivity is the prime parameter for electrocatalytic activity. The phosphides are metallic in nature and highly conductive[1]. In the present case, the post OER sample is cobalt oxyhydroxide enriched-CoP. After prolonged OER catalysis, the CoP (under the surface of Co-OOH) has been reduced with the increase of oxide/oxyhydroxide. The oxyhydroxide counterparts is comparatively poor conductive in nature[2], thus the performance of post-OER samples are degraded.

References:

1. A. Dutta and N. Pradhan, *J. Phys. Chem. Lett.*, 2017, **8**, 144–152.
2. M. Miao, R. Hou, R. Qi, Y. Yan, L. Q. Gong, K. Qi, H. Liu and B. Y. Xia, *J. Mater. Chem. A*, 2019, **7**, 18925–18931

Table S1. A comparison of CoP/MXene OER performance with latest reported OER electrocatalysts in alkaline medium.

Electrocatalysts	Electrolyte	$\eta_{10\ mA\ cm^{-2}}$ (mV)	Tafel slope (mV dec^{-1})	Reference
CoP/MXene	**1 M KOH**	**230**	**32.5**	**This work**
CoP/NCNHP	1 M KOH	310	70	J. Am. Chem. Soc. **2018**, 140, 2610.
S-$Co_{9-x}Fe_xS_8$@rGO	0.1 M KOH	290	66	Small. **2018**, 14, 1703748.
HG-$NiFe_x$	1 M KOH	310	39	Sci. Adv. **2018**, 4, eaap7970.
Ni-NHGF	1 M KOH	331	63	Nat. Catal.**2018**, 1, 63.
Co/CoP-5	1 M KOH	283	79.5	Adv. Energy Mater. **2017**, 7, 1602355.
Fe_1Co_1NS	0.1 M KOH	308	36.8	Adv. Mater.**2017**, 29, 606793.
NiCoP/C	1 M KOH	330	96	Angew.Chem.Int. Ed. **2017**, 56, 3897.
$MnCoPO_x$	1 M KOH	320	52	Angew. Chem.,Int. Ed. **2017**, 56, 2386.
NiFe-LDH/Co,N-CNF	0.1 M KOH	312	60	Adv. Energy Mater. **2017**, 1700467.
Ni_2P@C/G	1 M KOH	285	44	Chem.Commun., **2017**, 53, 8372.
IrMn/Fe_3Mo_3C	0.1 M KOH	290	89	Adv. Mater.**2017**, 29, 1702385.
Fe-CoP@Ti	1 M KOH	230	67	Adv. Mater. **2017**, 29, 1602441.
Co_3O_4@CoP	1 M KOH	238	51.4	Adv. Energy Mater. **2017**, 7, 1602643.
Co_4Ni_1P NTs	1 M KOH	245	61	Adv. Funct. Mater. **2017**, 27, 1703455.
$CoNi(OH)_x$	1 M KOH	280	77	Adv. Energy Mater. **2016**, 6, 1501661.
Co-Bi NS/G	1 M KOH	290	53	Angew. Chem.Int. Ed. **2016**, 55, 2488.
CoMnP	1 M KOH	330	61	J. Am. Chem. Soc. **2016**, 138, 4006.
Ni-P	1M KOH	300	64	Energy Environ. Sci. **2016**, 9, 1246.
FeP @ carbon fiber	1M KOH	350	63.6	Chem. Commun. **2016**, 52, 8711.
CoP/Graphene	1M KOH	340	66	Chem. Sci. **2016**, 7, 1690.
$NiCo_{2.7}(OH)_x$	1 M KOH	350	65	Adv. Energy Mater. **2015**, 5, 1401880.
CoP	1 M KOH	345	47	Angew. Chem. Int. Ed. **2015**, 127, 6349.
CoP/CNT	1M KOH	330	40	ACS Appl. Mater. Inter. **2015**, 7, 28412.
CoP /C	1M KOH	320	84	ACS Catal. **2015**, 5, 6874.
NiCoO	1 M KOH	340	51	Adv. Energy Mater. **2015**, 5, 1500091.
CoP-MNA	1 M KOH	290	65	Adv. Funct. Mater. **2015**, 25, 7337.

Table S2. Summary of the OER performance, C_{dl}, ECSA and RF for different electrocatalysts measured in 1 M KOH.

Electrocatalysts	$\eta_{10mA\ cm^{-2}}$ (mV)	Tafel slope (mV dec^{-1})	C_{dl} (mF/cm^2)	ECSA	RF	Relative ECSA
CoP/MXene	230	50	11	275	275	7.8
Co_7Se_8/MXene	291	81.5	2.5	62.5	62.5	1.8
CoP	280	56.5	5.7	142.5	142.5	4
Co_7Se_8	325	97	1.4	35	35	1

Note: RF = ECSA/Geometrical area of electrode (1.0 cm^2)

Table S3. Summary of Impedance parameters obtained by fitting the experimental data in Fig. S7.

Electrocatalyst	R_s (Ω cm^2)	R_1 (Ω cm^2)	R_2 (Ω cm^2)
CoP	1.91	0.65	4.31
CoP/MXene	2.30	0.43	1.72
Co_7Se_8	2.65	0.95	8.2
Co_7Se_8/MXene	1.90	0.60	3.35

Table S4. A comparison of CoP/MXene HER performance with recently reported electrocatalysts in alkaline medium.

Electrocatalysts	Electrolyte	$\eta_{10\ mA\ cm^{-2}}$ (mV)	Tafel slope (mV dec^{-1})	Reference
CoP/MXene	**1 M KOH**	**116**	**57**	**This work**
$Ni_{0.9}Fe_{0.1}PS_3$@ MXene	1 M KOH	196	114	Adv. Energy Mater. **2018**, 8, 1801127.
NiFe LDH-NS@Graphene	1 M KOH	300	110	Adv. Mater. **2017**, 29, 1700017.
CoP@NC	1 M KOH	129	58	ACS Catal.**2017**, 7, 3824.
Co/N-doped carbon	1 M KOH	260	91.2	ACS Nano **2016**, 10, 684.
$NiCo_2S_4$ NW/NF	1 M KOH	210	58.9	Adv. Funct. Mater. **2016**, 26, 4661.
CoP	1 M KOH	80	60	Nanotechnology **2016**,27 475702.
CoP	1 M KOH	110	70.9	Green Chem. **2016**, 18, 2287.
Ni/NiP	1 M KOH	130	58.5	Adv. Funct. Mater. **2016**, 26, 6785.
NiCoP	1 M KOH	43	59.4	ACS Appl. Mater. Inter. **2016**, 8, 34270.
$Ni_{0.5}1Co_{0.49}P$ film/NF	1 M KOH	82	43	Adv. Funct. Mater. 2016, 26, 7644.
Ni-Co-P	1 M KOH	150	60.1	Chem. Commun. **2016**, 52,1633.
CoO_x@CN	1 M KOH	232	115	J. Am. Chem. Soc. **2015**, 137,2688.
Co-P film/Cu	1 M KOH	94	42	Angew. Chem., Int.Ed. **2015**, 54, 625.

Table S5. Comparison of two electrode water splitting cell voltage of CoP/MXene with recently reported bifunctional electrocatalysts in alkaline medium.

Electrocatalysts	**Electrolyte**	**Overall voltage V @ 10 mA cm^{-2}**	**Reference**
CoP/MXene	**1 M KOH**	**1.56**	**This work**
NiCo-HS@G/NF// NiMo/NiCo-HS@G/NF	1 M KOH	1.51	Adv. Funct. Mater. **2018**, 28, 1704594.
NiFe/$Ni(OH)_2$/NiAl // NiMo/$Ni(OH)_2$/NiAl	1 M KOH	1.59	Adv. Sci. **2017**, 4, 1700084.
Ni_3Se_2/NF // $NiCo_2S_4$/NF	1 M KOH	1.58	Appl. Catal., B **2017**, 203, 485.
NiCoP	1 M KOH	1.52	ACS Catal. **2017**, 7, 4131.
EG/$Co_{0.85}$Se/NiFe-LDH	1 M KOH	1.67	Energy Environ. Sci. **2016**, 9, 478.
NiCoP/rGO	1 M KOH	1.59	Adv. Funct. Mater. **2016**, 26, 6785.
$NiCo_2O_4$/NF	1 M KOH	1.84	Adv. Funct. Mater. **2016**, 26, 4661.
Ni(2.3%)-CoS_2	1 M KOH	1.66	Elelctrochem. Commun. **2016**, 63, 60.
NiS	1 M KOH	1.64	Chem. Commun. **2016**, 52, 1486.
Ni_3S_2/MoS_2	1 M KOH	1.56	Angew. Chem., Int. Ed. **2016**, 55, 6702.
Ni_xP_y	1 M KOH	1.57	ACS Appl. Mater. Interfaces **2016**, 8, 10826.
Ni-P	1 M KOH	1.67	ChemCatChem **2016**, 8,106.
$NiCo_2S_4$	1 M KOH	1.68	Nanoscale **2015**, 7, 15122.
Ni_3Se_2	1 M KOH	1.65	Catal. Sci. Technol. **2015**, 5, 4954.
Ni_2P	1 M KOH	1.63	Energy Environ. Sci. **2015**, 8, 2347.

Table S6. Summary of Impedance parameters obtained by fitting the experimental data in Fig. S6.

Electrocatalyst	R_s (Ω cm^2)	R_1 (Ω cm^2)	R_2 (Ω cm^2)
CoP/MXene	2.30	0.43	1.72
CoP/MXene (Post-OER)	1.90	0.61	3.46
Co_7Se_8/MXene	1.90	0.60	3.35
Co_7Se_8/MXene (Post-OER)	2.82	2.97	16.2
Co(OH)F/MXene	2.92	0.60	2.71
Co(OH)F/MXene (Post-OER)	3.16	0.61	5.18