Electronic Supplementary Information†

For

Phosphorus-decorated Mo-MXene/CQD hybrid: a 2D/0D architecture for bifunctional electrochemical water splitting

Atanu Panda [a], Hansang Kim [a]*

[a] Department of Mechanical Engineering, Gachon University, Gyeonggi-do 13120, Republic of Korea

Corresponding Authors

*E-mail: hskim70@gachon.ac.kr

Chemicals:

MAX phase of Mo_2AlC_2 were purchased from China (Beijing Dingsheng Brothers Technology

Co., Ltd). Phloroglucinol, Lithium floride (LiF), Monosodium phosphate (NaH_2PO_4), potassium hydroxide (KOH), 10% Nafion solution were purchased from Sigma- Aldrich (Canada) and used as received. High-purity Sulfuric acid, Sodium sulfate, hydrochloric acid was purchased from Sigma- Aldrich (Canada). Pure water was obtained using a NanoPure system and was used in the preparation of all solutions. Electrochemical experiments were carried out in 0.5 M (~pH 0) H_2SO_4 solution.

Characterizations:

The wide-angle powder X-ray diffraction (XRD) measurement was carried out on a Rigaku X-ray diffractometer (X-ray generator output: 3KW (target material Cu), 20-60kW, 2-60mA) with scan rate of 4^o/min. The morphology of the catalysts was observed by field-emission scanning electron microscopy (FESEM) on a JEOL (JSM-7500F, 1.0nm at 15kV). The morphology of the sample was acquired on a Tecnai 2010 (Japan) transmission electron microscope (TEM) at 300 kV with resolution: 1.4Å (Fully embedded High Angle Annular Dark Field (HAADF) detector-HR STEM resolution). The Raman spectroscopy were analysed on Witec (Alpha 300M+) instrument fitted with 600 nm wavelength. X-ray photoelectron spectroscopy (XPS) was analyzed on an Multilab-2000 X-ray photoelectron spectrometer (Al K Alpha, Lens Mode-LAXPS, step size 0.100 eV). The solid-state NMR spectroscopy were performed by using AVANCE III HD (400 MHz, Bruker, Germany, Spinning rate: 14 kHz,). All electrochemical experiments were performed in compact type electrochemical workstation ZIVE SP1 equipped with Smart Manager (SM) Software package.

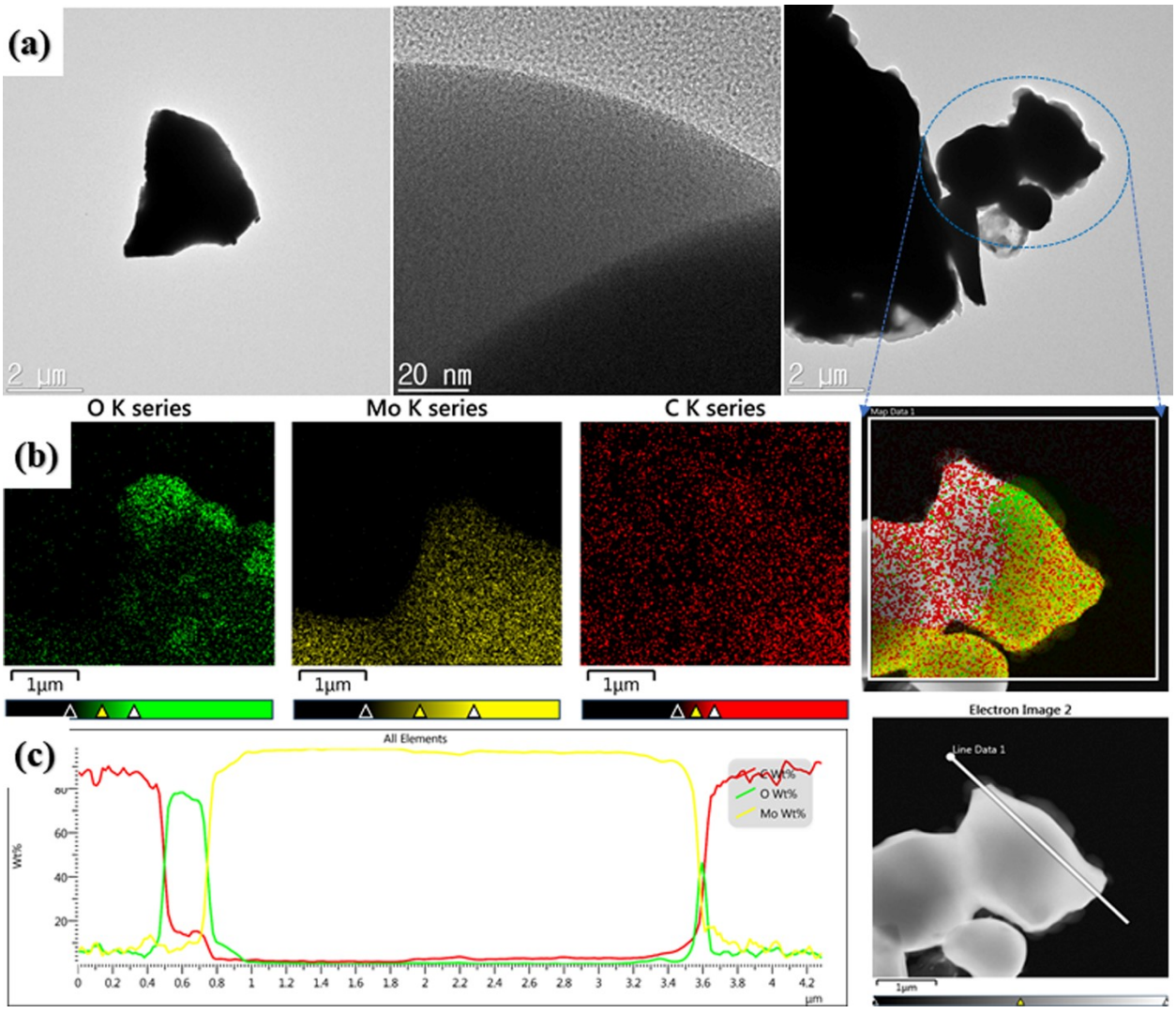

Fig. S1. TEM and elemental mapping of 2D Mo-MXene sheet.

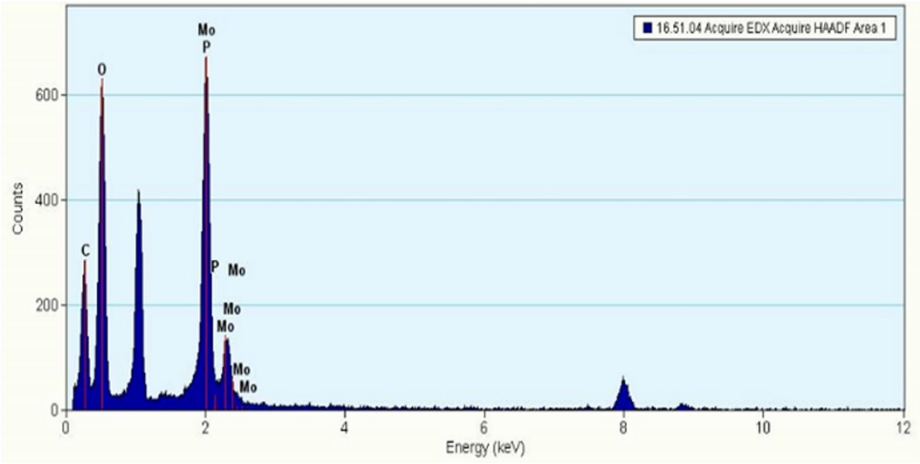

Fig. S2. EDAX analysis of Mo-MX/C/P hybrid.

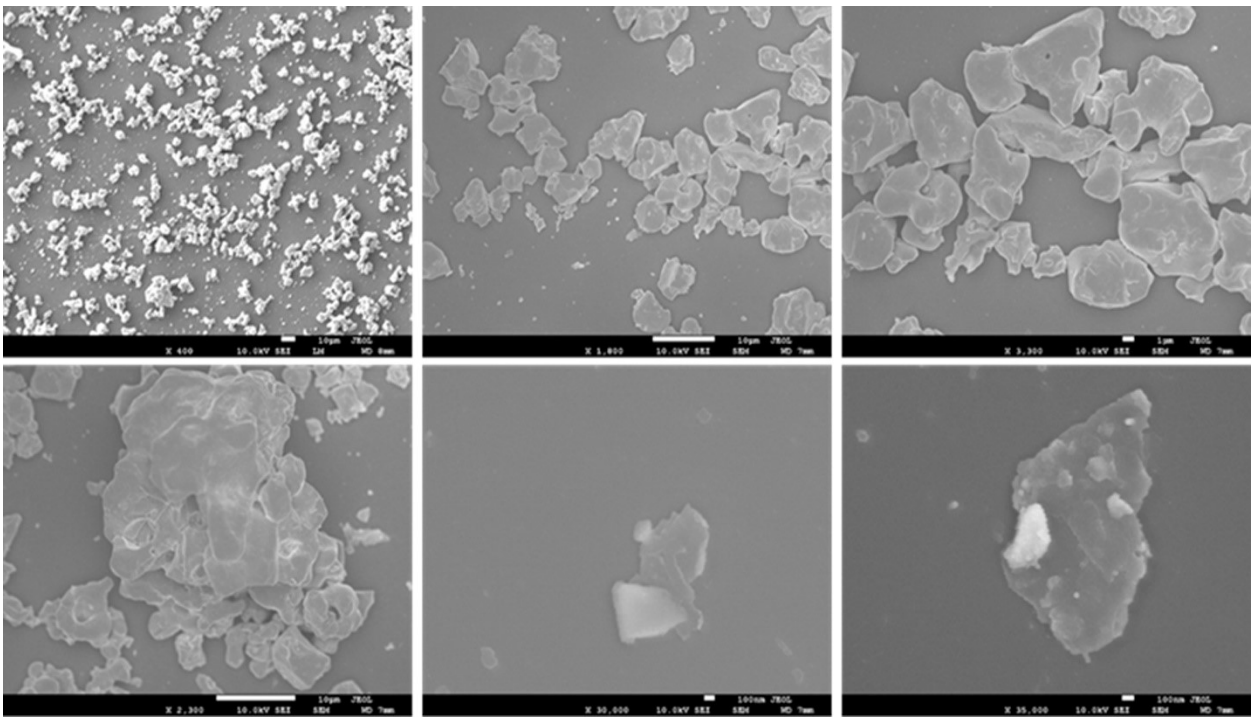

Fig. S3. Fe-SEM of 2D Mo-MXene sheet.

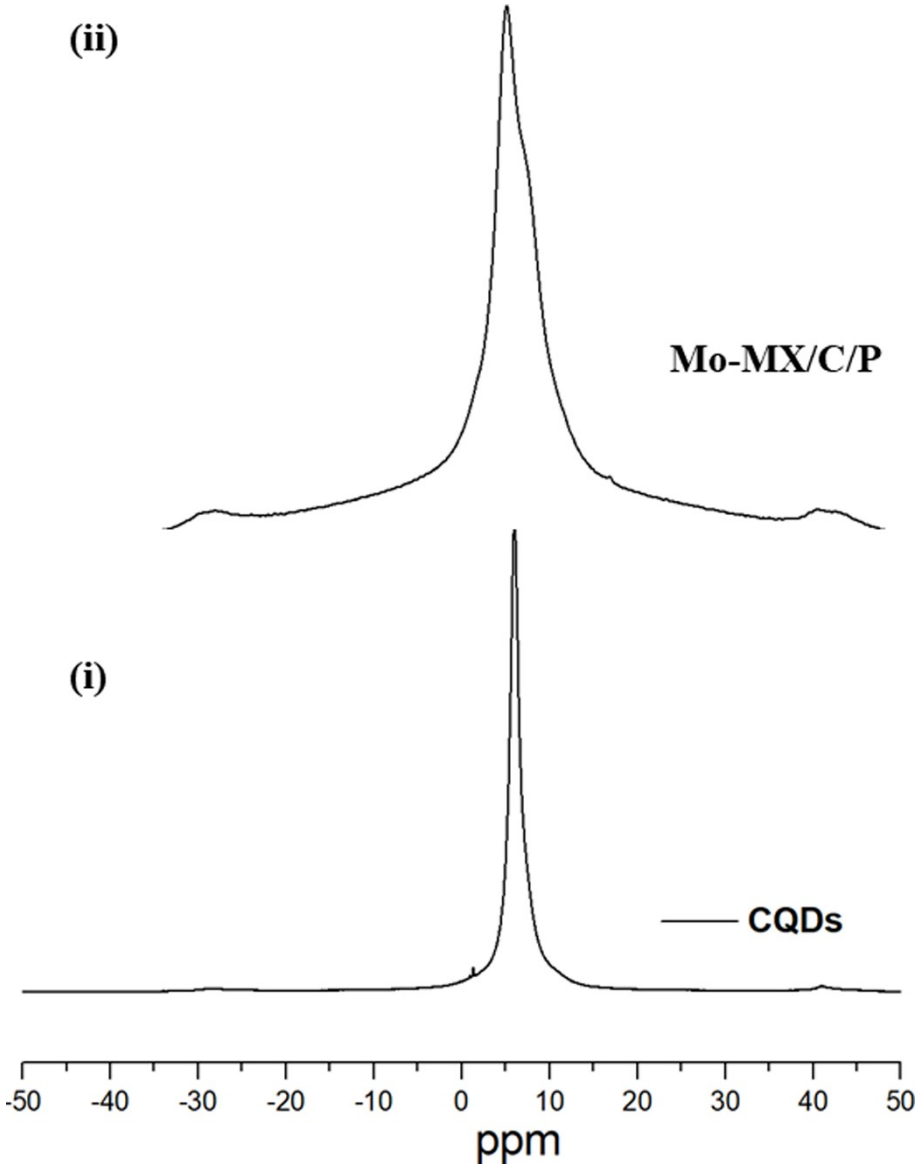

Fig. S4. 1H proton NMR CQDs and Mo-MX/C/P hybrid.

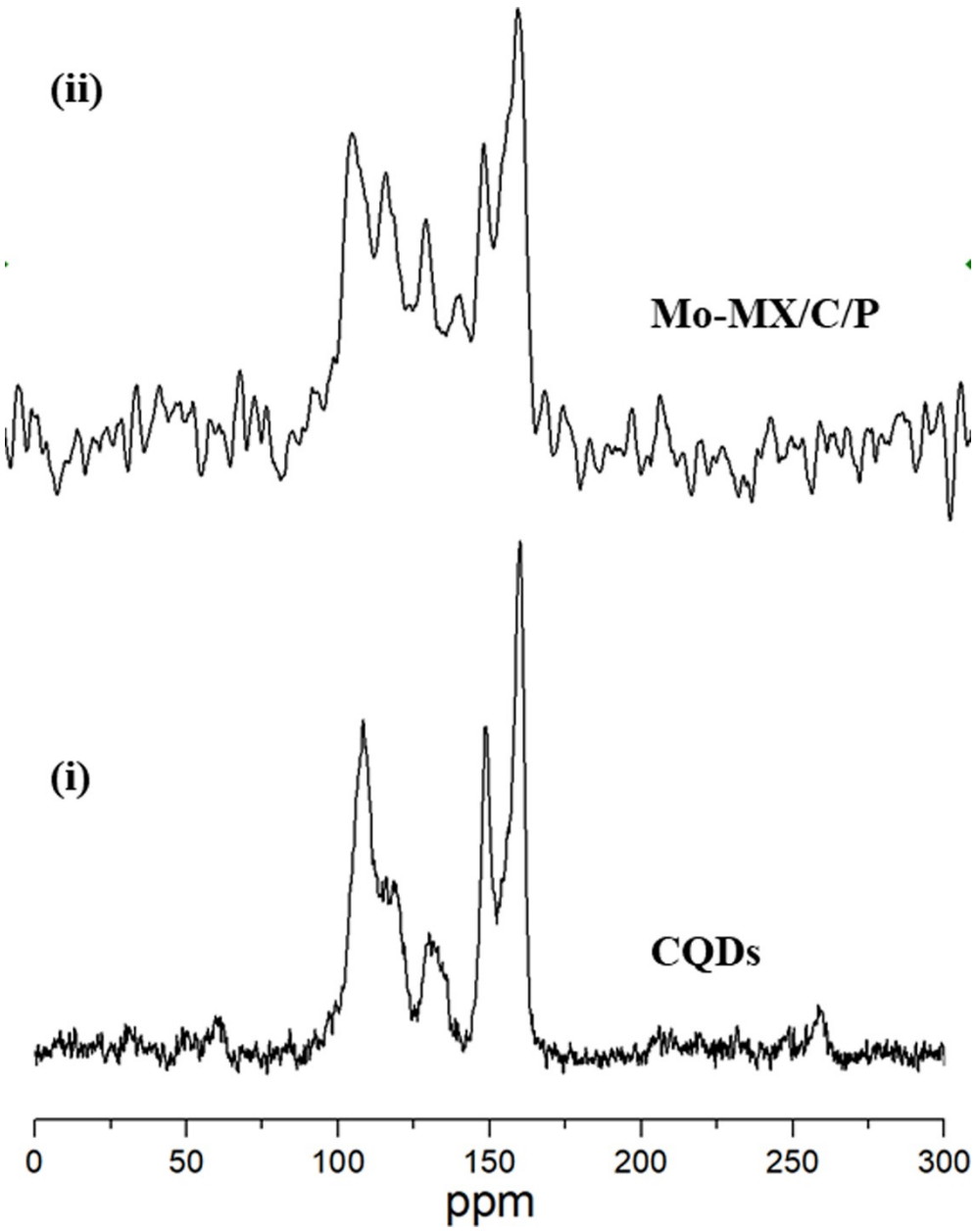

Fig. S5. 13C NMR CQDs and Mo-MX/C/P hybrid.

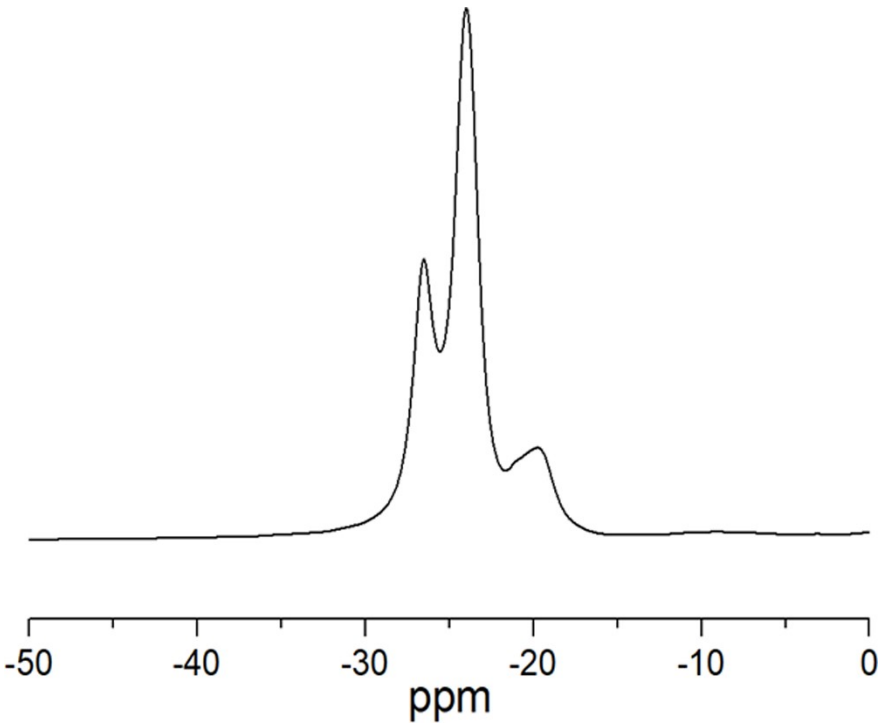

Fig. S6. 31P NMR of Mo-MX/C/P hybrid.

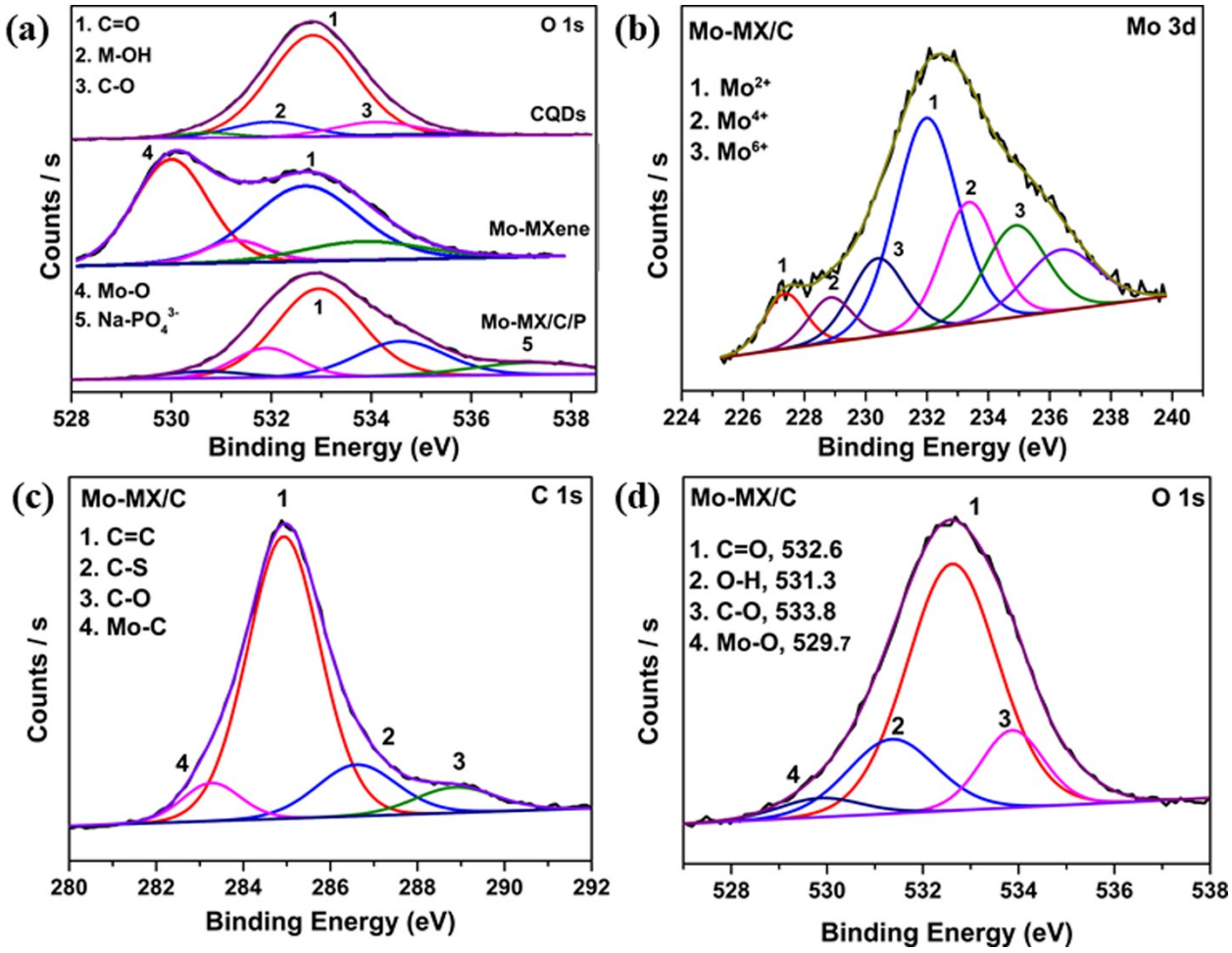

Fig. S7. XPS survey spectra of (a) O1s for CQDs, Mo-MXene and Mo-MX/C/P; ((b)–(d)) High-resolution normalized XPS spectra for the following: (b) Mo 3d, (c) C 1s, (d) O 1s of Mo-MX/C hybrid.

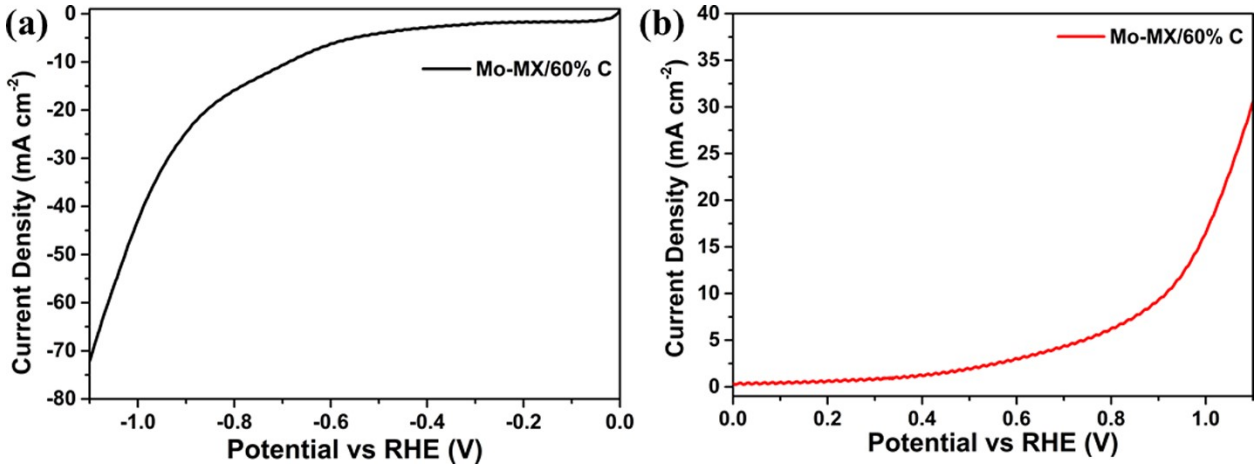

Fig. S8. (a) HER polarization curves, (b) OER polarization curves of Mo-MX/60 % C.

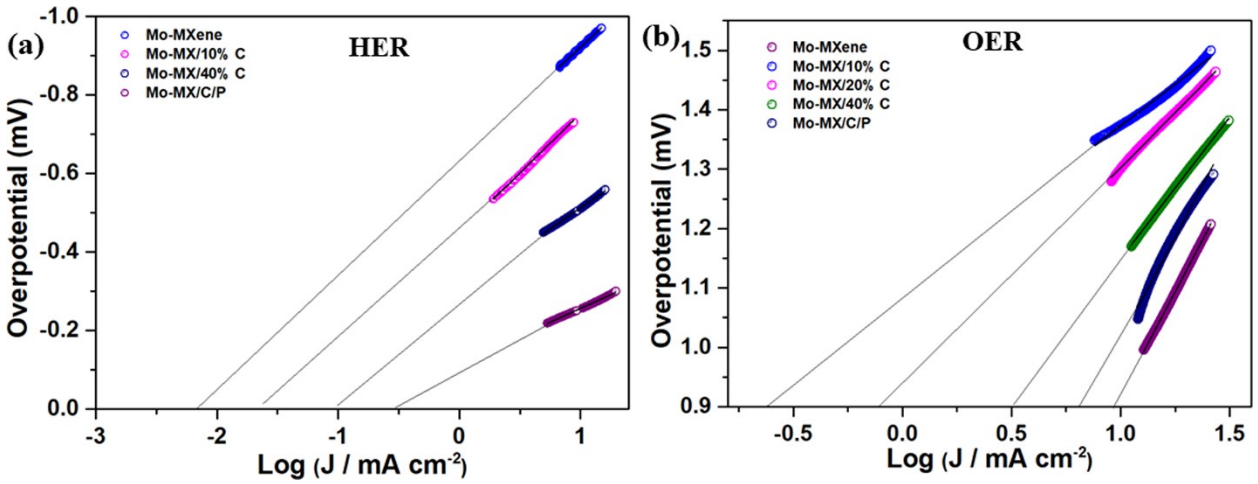

Fig. S9. The exchange current density (j_0) for (a) HER and (b) OER.

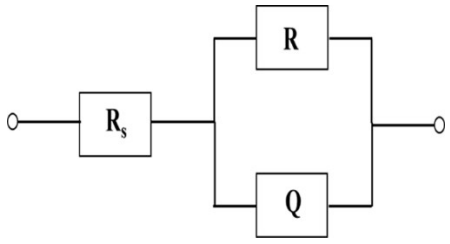

Fig. S10. Fitted electronic circuit model obtained for EIS spectroscopy by using ZAMAN impedance electrochemical software.

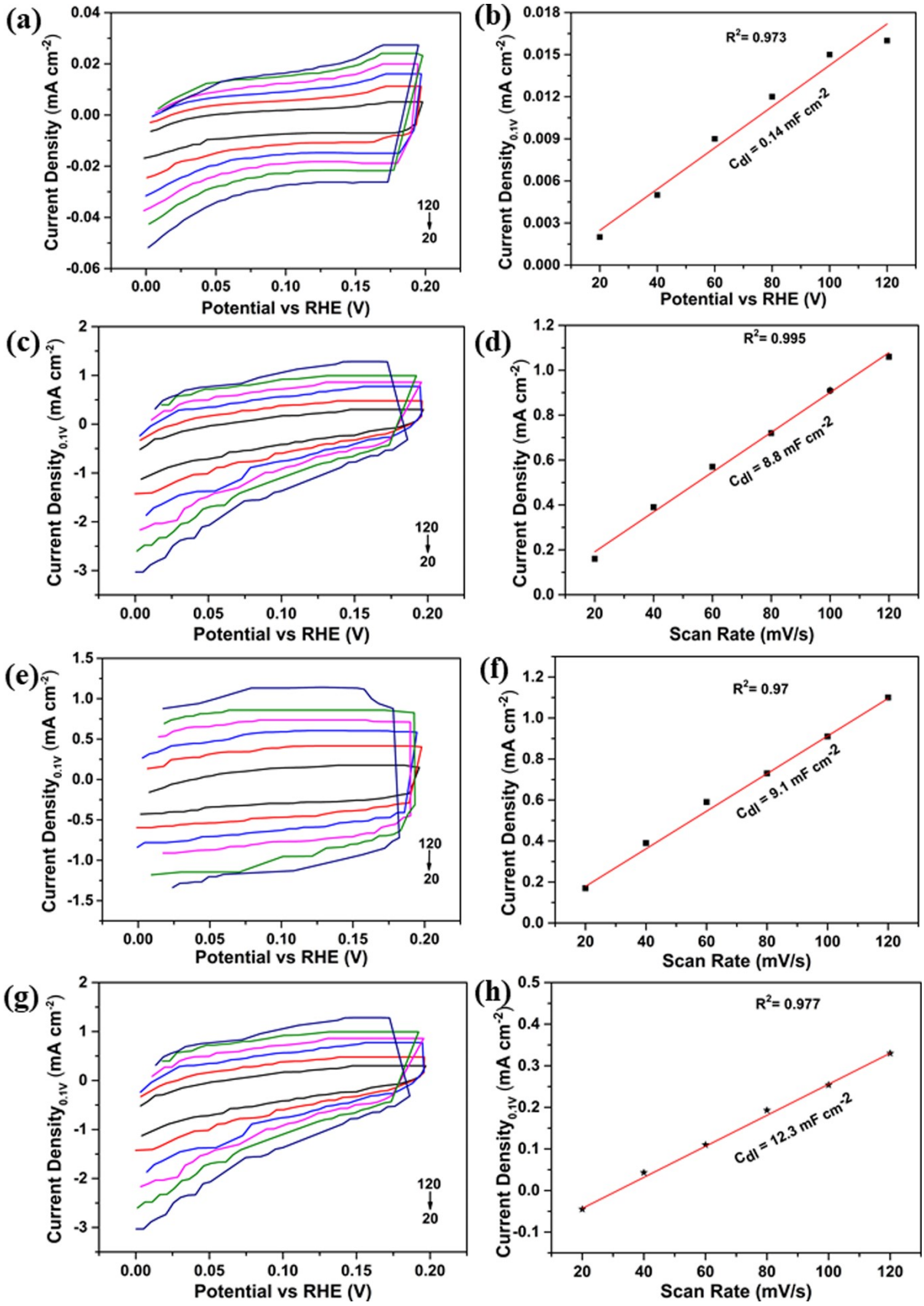
(a)
Current Density (mA cm-2)
Potential vs RHE (V)
120
20
(b)
R2= 0.973
Cdl = 0.14 mF cm-2
Current Density0.1V (mA cm-2)
Potential vs RHE (V)
(c)
Current Density0.1V (mA cm-2)
Potential vs RHE (V)
120
20
(d)
R2= 0.995
Cdl = 8.8 mF cm-2
Current Density (mA cm-2)
Scan Rate (mV/s)
(e)
Current Density0.1V (mA cm-2)
Potential vs RHE (V)
120
20
(f)
R2= 0.97
Cdl = 9.1 mF cm-2
Current Density (mA cm-2)
Scan Rate (mV/s)
(g)
Current Density0.1V (mA cm-2)
Potential vs RHE (V)
120
20
(h)
R2= 0.977
Cdl = 12.3 mF cm-2
Current Density0.1V (mA cm-2)
Scan Rate (mV/s)

Fig. S11. Double layer capacitance and respective CVs of (a) bare CPE electrode, (c) CQDs, (Mo-MXene), (e) Mo-MX/C and (g) Mo-MX/C/P hybrid from scan rate 20-120 mV s^{-1}.

The electrochemical surface area (ECSA) was calculated. using the following formula:

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

Where C_{dl} is double layer capacitance of electrode-electrolyte interaction. C_s is the specific capacitance and equal to 0.040 mF cm^{-2}. The roughness factor (RF) was calculated using the following relationship.

$$RF = ECSA / \text{geometric area of the electrode}$$

Where electrode geometric area is 1 cm^2.

Table S1: Summarization of electrochemical active surface area.

Catalysts	Double layer capacitance (C_{dl})	Electrochemical active surface area (ECSA)	Roughness factor (RF)
CPE	0.14 mF cm^{-2}	3.5	3.5
CQDs	8.8 mF cm^{-2}	220	220
Mo-MXene	9.1 mF cm^{-2}	227	227
Mo-MX/C	12.3 mF cm^{-2}	307	307
Mo-MX/C/P	65.1 mF cm^{-2}	1627	1627

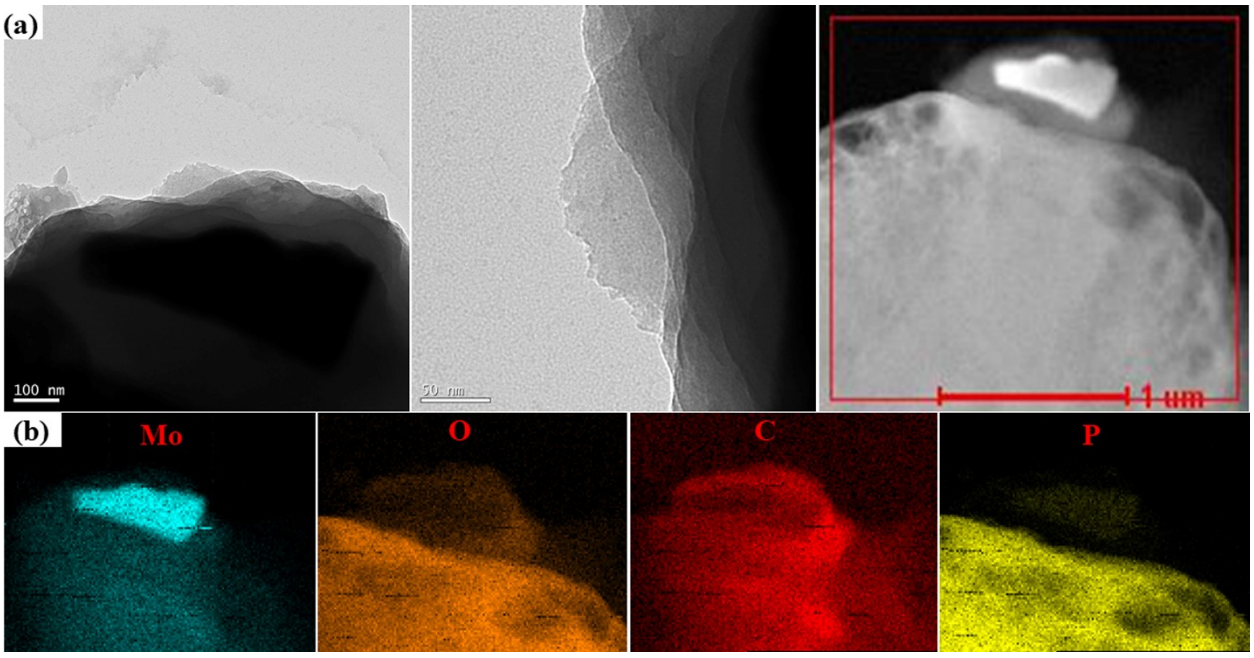

Fig. S12. (a) TEM and HR-TEM, (b) elemental mapping of Mo-MX/C/P hybrid after 10 hours durability test in 0.5 M H_2SO_4 solution.

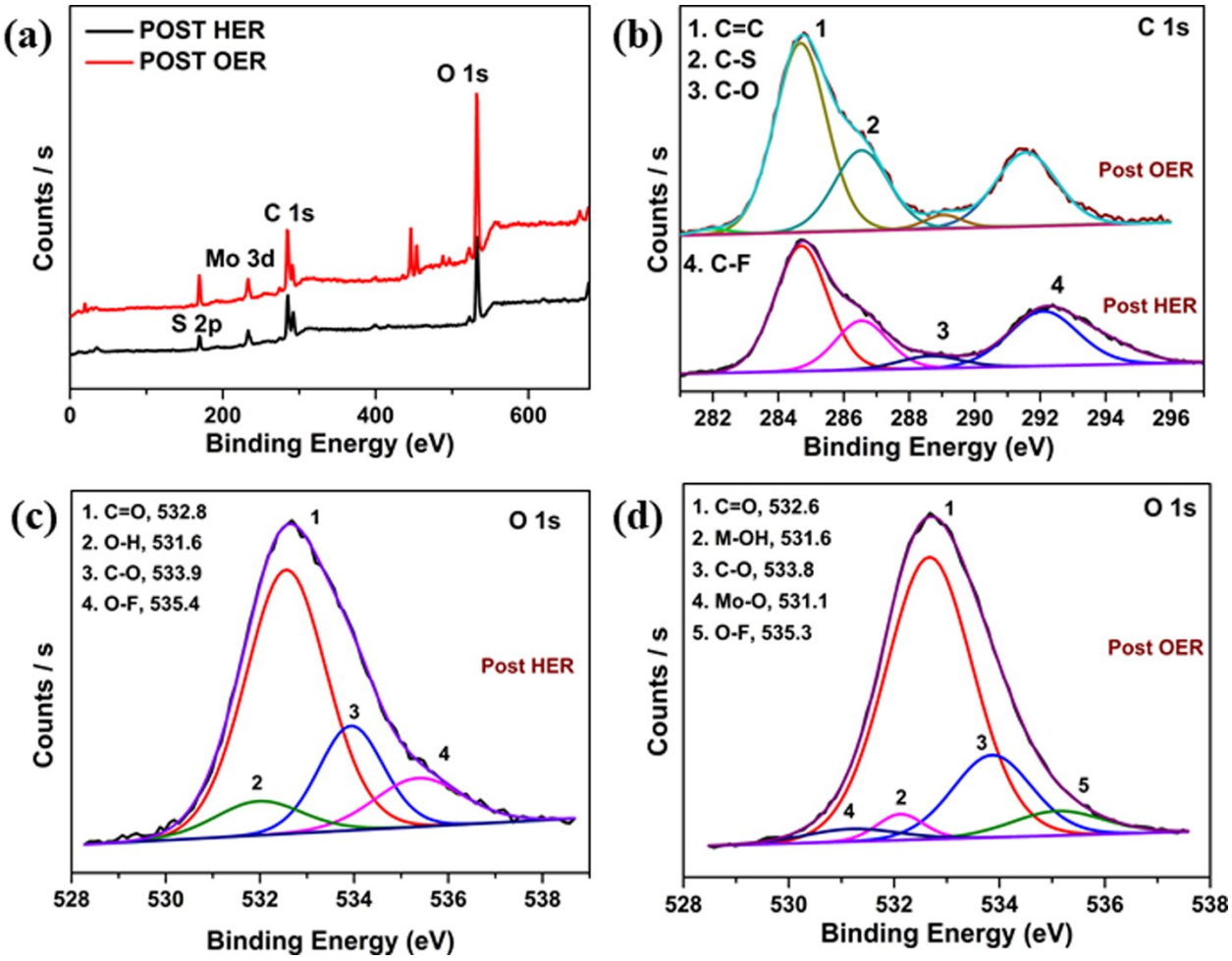

Fig. S13. (a) XPS survey spectra. ((b)–(d)) High-resolution normalized XPS spectra for the following: (b) C 1s, (c) O 1s after HER, (d) O 1s after OER of Mo-MX/C/P hybrid.

Note: The XPS of post water electrolysis were done by using FTO as working electrode.

Table S2. Summary of Mo-based catalysts for electrochemical HER.

Catalyst	Loading amount mg/cm^2	Current density (mA cm^{-2})	Overpotential (mV)	electrolyte	Reference
MoN	0.285	38.5	300	0.5 M H_2SO_4	*Chem. Sci. 2014, 5, 4615.*
MoB	2.5	17	250	0.5 M H_2SO_4	*Angew. Chem. Int. Ed.2012, 51, 12703.*

$(MoS_2)_{0.6}(SnO_2)_{0.4}$/rGO	0.27	10	263	0.5 M H_2SO_4	*ACS Appl. Mater. Interfaces.2017, 9, 8065.*
$Mo_{0.21}W_{0.79}S_2$	NA	10	346	0.5 M H_2SO_4	*Adv. Mater. Interfaces 2015, 2, 1500041*
MoP/CF	NA	10	200	0.5 M H_2SO_4	*Appl. Catal. B-Environ. 2015, 164, 144.*
$MoS_{1.5}Se_{0.5}$	0.18	10	383	0.5 M H_2SO_4	*Nanoscale 2014, 6, 12856*
N, P-doped Mo_2C@C	0.9	10	141	0.5 M H_2SO_4	*ACS Nano 2016, 10, 9, 8851.*
MoSx@Mo_2C	0.21	178	400	0.5 M H_2SO_4	*ACS Catal. 2015, 5, 6956.*
MoC–Mo_2C	0.14	10	126	0.5 M H_2SO_4	*Chem. Sci. 2016, 7, 3399.*
MoS_2/Mo_2CTx	NA	10	112	1 M KOH	*Nanoscale, 2019, 11, 10992*
Mo_2CTx/2H-MoS_2	NA	10	119	1 M KOH	*ACS Nano, 2020, 14, 16140*
Mo-Mxene/C/P hybrid	0.25	10	58	0.5 M H_2SO_4	***This work***