Supplementary Document

Construction of MXene/MIL Fe-53/ZIF-67 derived bifunctional electrocatalyst for efficient overall water splitting

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Materials

MAX phase (Ti_3AlC_2), acquired from Nanoshel, UK. Hydrofluoric acid (HF), Dimethyl formamide (DMF), ferric chloride hexahydrate ($FeCl_3.6H_2O$), 2-aminoterephthalic acid (NH_2-BDC), ***cobalt(II) nitrate hexahydrate (***$Co(NO_3).6H_2O$), 2-methyl imidazole ***($C_4H_6N_2$)*** and methanol were purchased from Macklin chemicals, China. RuO_2 (99.9 %) and Nafion solution (5 % wt.) were purchased from Sigma-Aldrich.

Characterizations

X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance diffractometer, employing Cu-Kα radiation at a scan rate of 5°/min and a step size of 0.02°. The morphological analysis was conducted via field emission scanning electron microscopy (FE-SEM) on a Philips XL-30, equipped with energy-dispersive X-ray spectroscopy (EDX). Measurements were performed in high vacuum mode with an acceleration voltage of 20 kV. To minimize charging effects, samples were gold-coated prior to analysis. Transmission electron microscopy (TEM) images were acquired using a JOEL 2100 microscope. Samples were prepared by sonication in 100% ethanol for 10 minutes and then deposited on holey carbon grids. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos Axis Ultra system, utilizing a monochromatic Al Kα X-ray source with an emission current of 10 mA and an anode potential of 15 kV.

Electrochemical evaluations

Electrochemical workstation, CHI 660E, containing three-electrode system was employed to perform the electrocatalytic measurements. The system was coupled with a rotating disk electrode (RDE). In the three-electrode system, the catalyst modified glassy carbon electrode (GCE) as working electrode, Platinum wire as counter electrode and Hg/HgO as used as reference electrode. The catalyst ink was prepared by sonicating 1 mg of testing catalyst with 80 μL isopropanol, 10 μL water/ethanol solution and 10 μL of 5% Nafion solution. Later, 5 μL of the prepared slurry was drop casted on the freshly polished GCE and dried at room temperature. For the oxygen evolution measurement, all linear sweep voltammetry (LSV) were recorded in O_2 saturated 1 M KOH electrolyte with a scan rate of 5 mVs^{-1} while for HER, 0.5 M H_2SO_4 electrolyte, without purged oxygen, was used. The Nernst formula was used to convert all the potential values to reversible hydrogen electrode (RHE): $E_{\mathrm{RHE}} = E_{\mathrm{Hg/HgO}} + 0.059\ \mathrm{pH} + 0.098$. Electrochemical impedance spectroscopy (EIS) was conducted at 1 V vs. RHE over 0.1 Hz to 100 kHz to estimate the charge transfer resistance. Cyclic voltammetry (CV) cycles in a non-faradaic potential range at scan rates of 10-100 mV s^{-1} were used to determine the electrical double-layer capacitance (C_{dl}) by linearly fitting the plot of current density versus scan rate.

Mass activity, Turn over frequency calculations

Mass activity

The catalytic performance of our desired catalyst was also checked through mass activity which was calculated by using following equation [1, 2]

Mass activity = j/m,

where j is the measured current density at decided overpotential i.e 250 mV and m is the catalyst loaded on glassy carbon electrode (0.28 $mgcm^{-2}$).

Turn over frequency (TOF)

TOF is defined as the number of reaction products generated per active site per unit time. TOF can be calculated from equation as given below [1, 2].

$$TOf = \frac{j.A}{4.F.m}$$

Where,

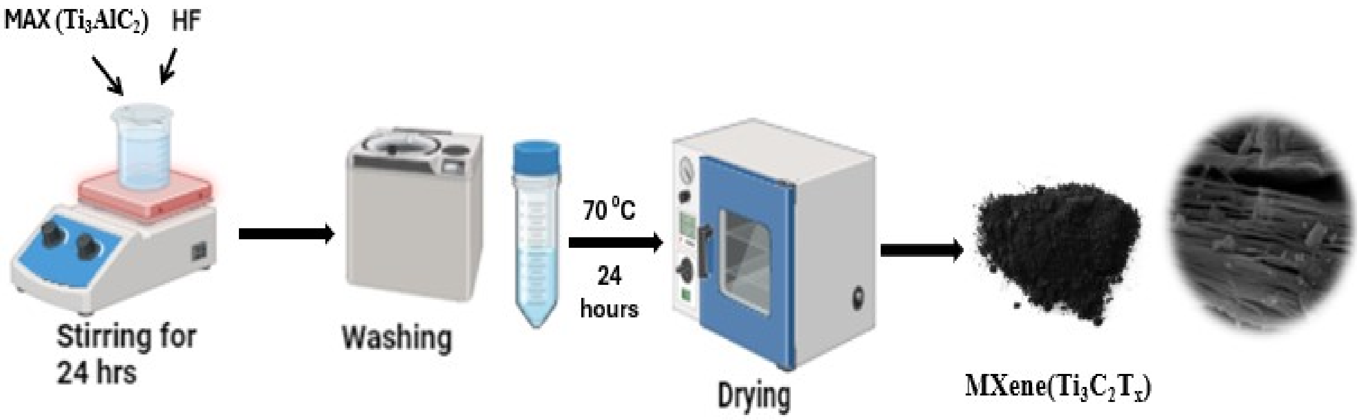
j = current density at a given overpotential (e.g., η=250 mV)

A_{geo} = geometric surface area of electrode (eg, 0.071 cm^2)

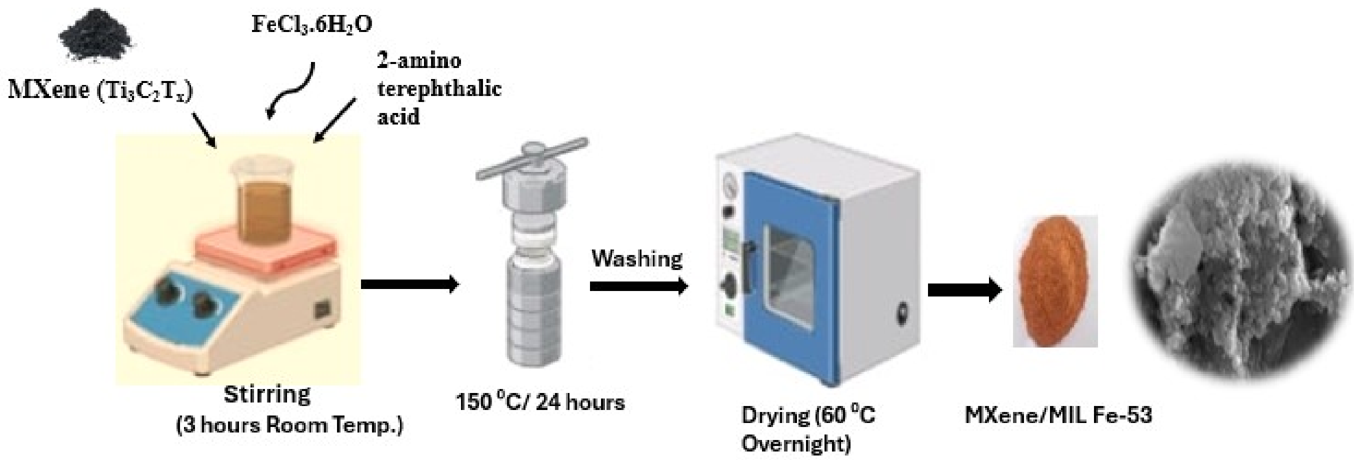
value 4 represent the transfer of 4 electrons per mole of O2 (for OER)/ the transfer of 2 electrons per mole of H2 (for HER)

F= Faraday's constant (96485 C/mol)

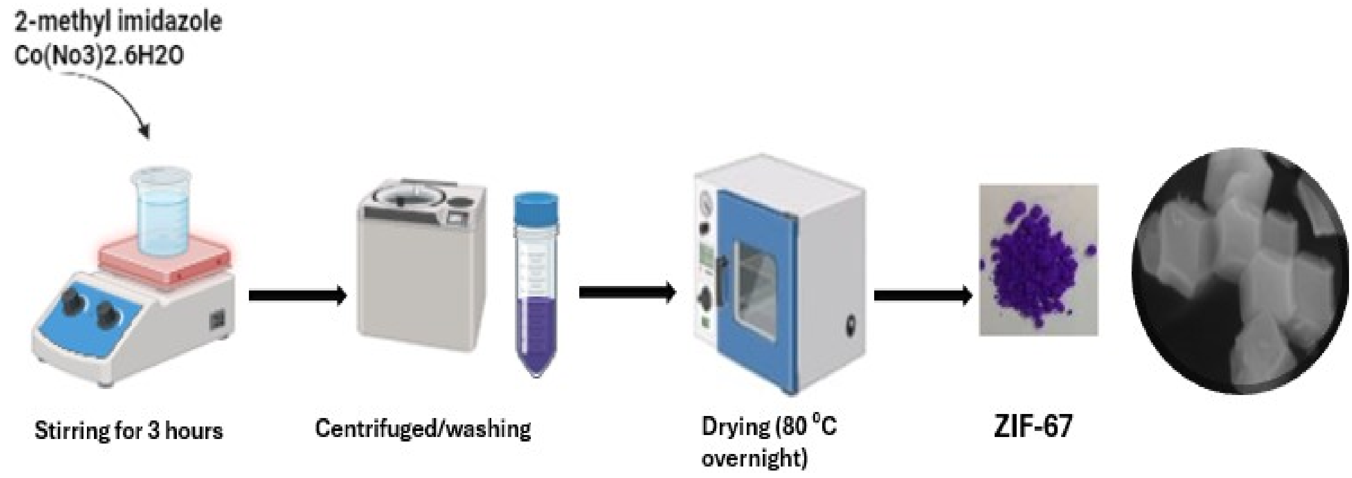
m is the moles of metal atoms present OR number of active sites.



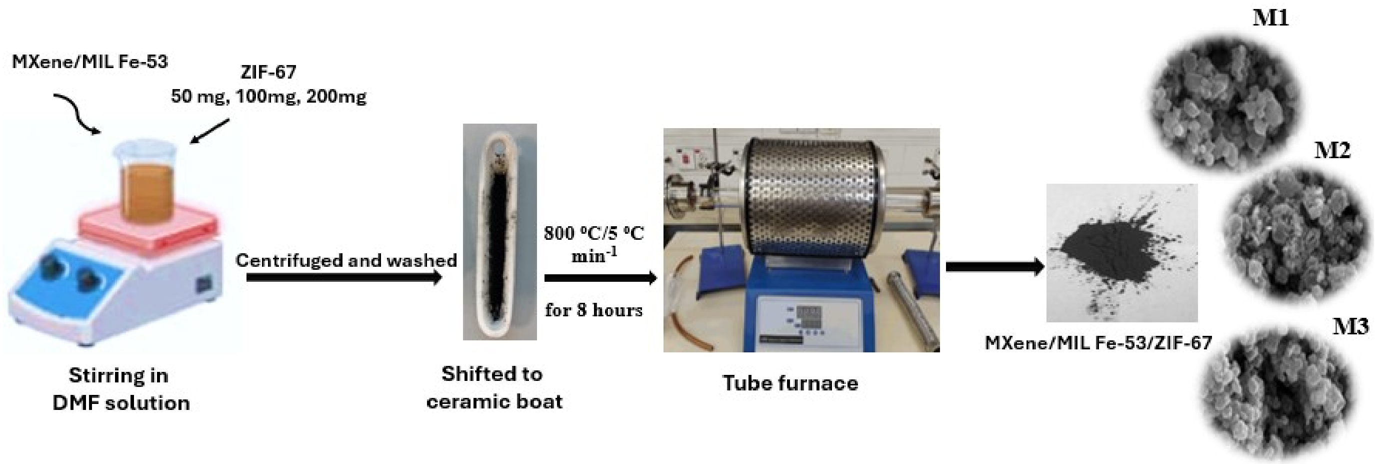
Scheme S1 synthesis scheme for MXene preparation from MAX phase.



Scheme S2 Synthesis scheme for MILFe53/MXene hybrid preparation



Scheme S3 Synthesis scheme for Zif67 preparation



Scheme S4. Schematic diagram for the synthesis of MXene/MIL Fe-53/ZIF67 composite.

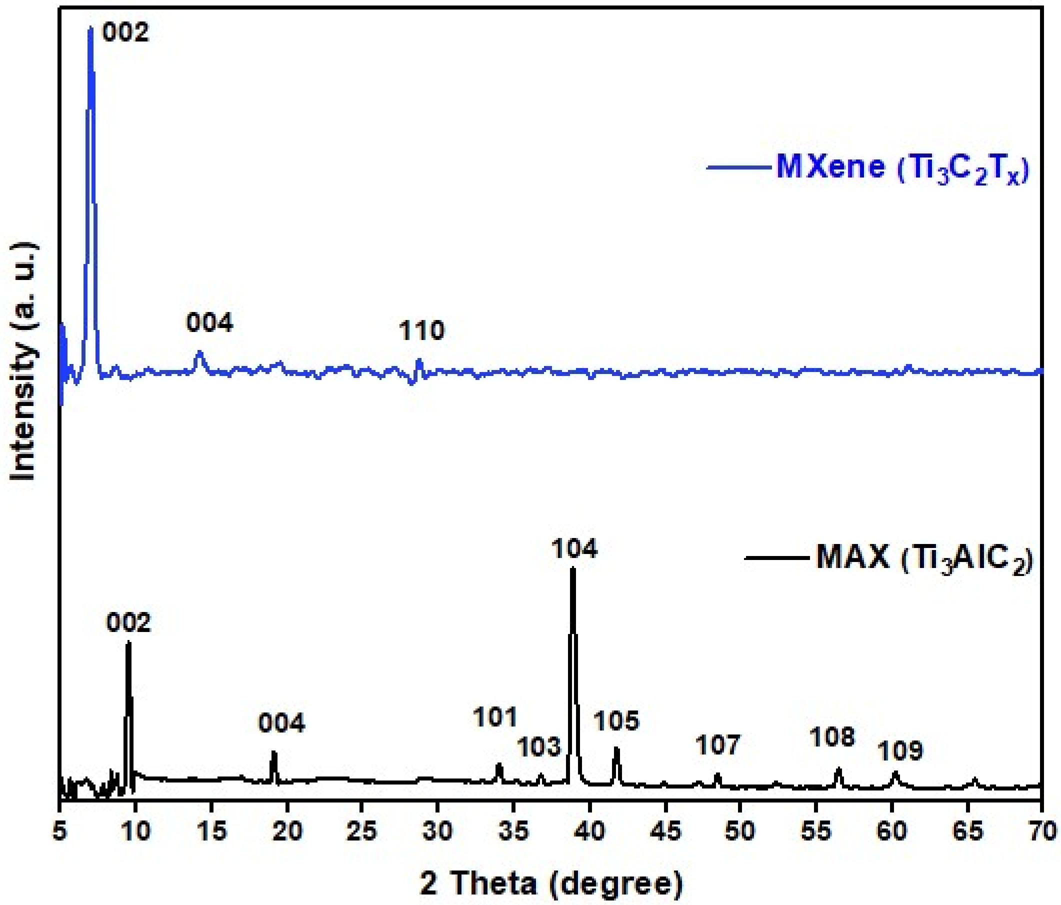


Figure S1. XRD pattern of MAX (Ti_3AlC_2) and MXene ($Ti_3C_2T_x$).

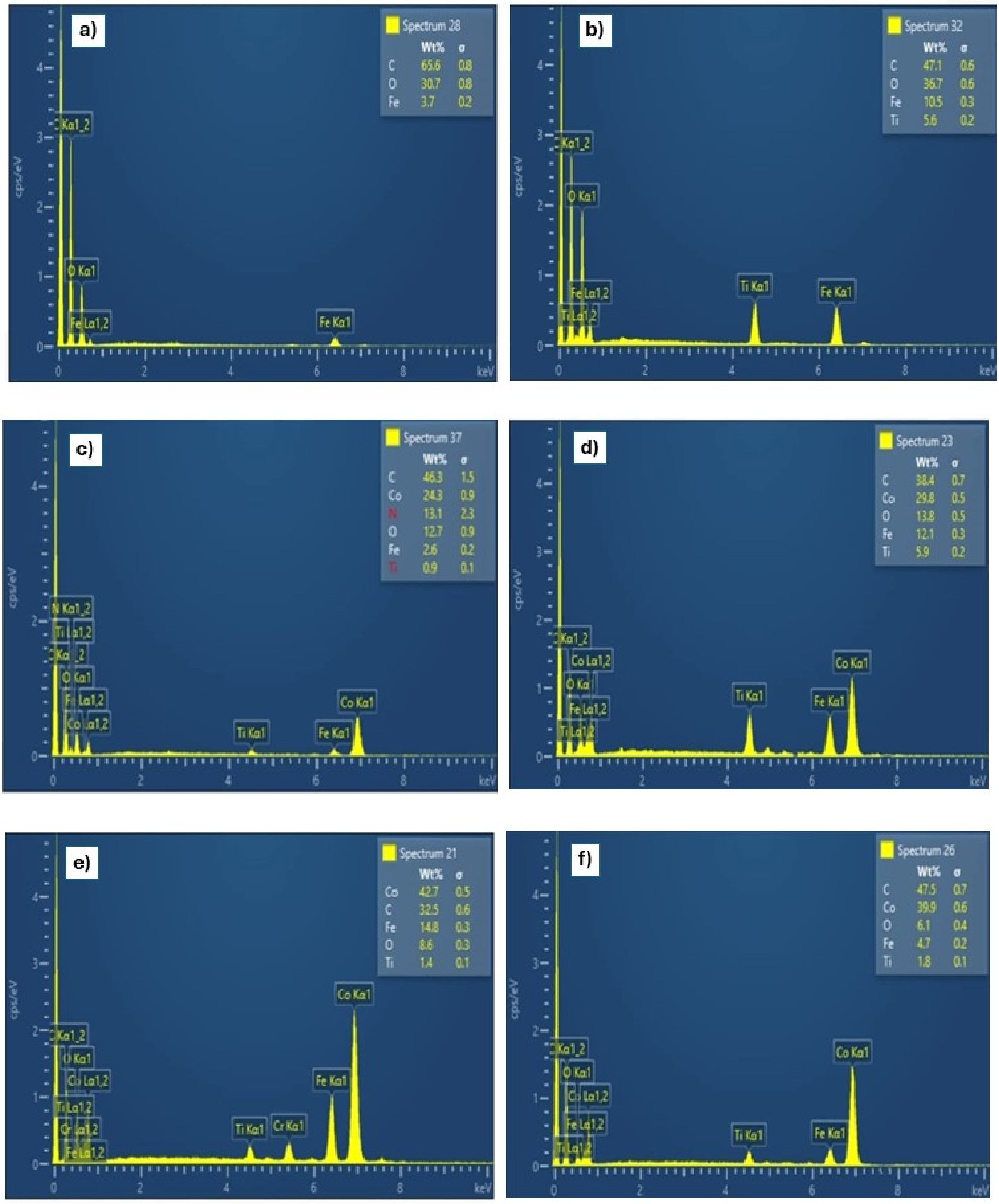


Figure S2. EDX element analysis of (a) Mil-53 (Fe), (b) MILMX, (c) MXMILZIF, (d) M1, (e) M2 and (f) M3.

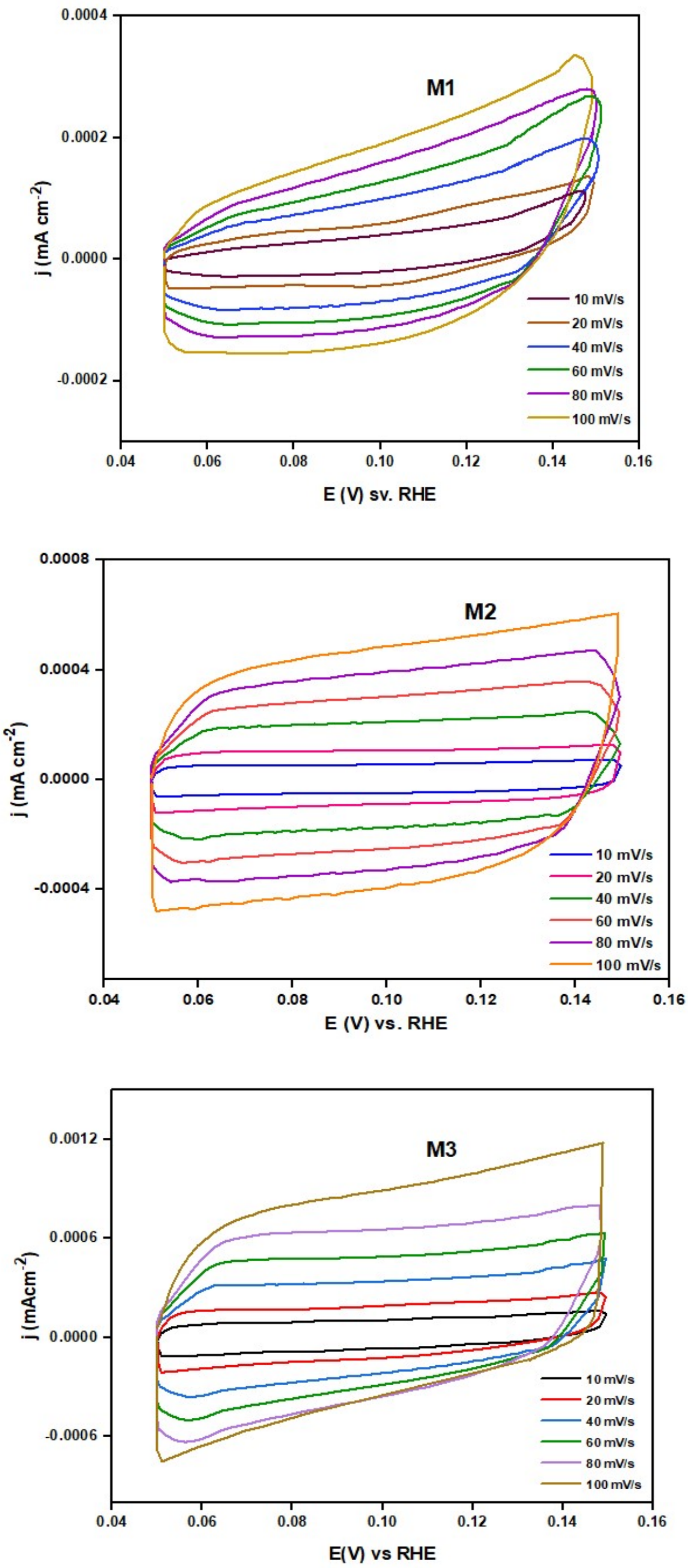


Figure S3. Non-faradic region cyclic voltammogram at various scanning rates of (a) M1, (b) M2 and (c) M3.

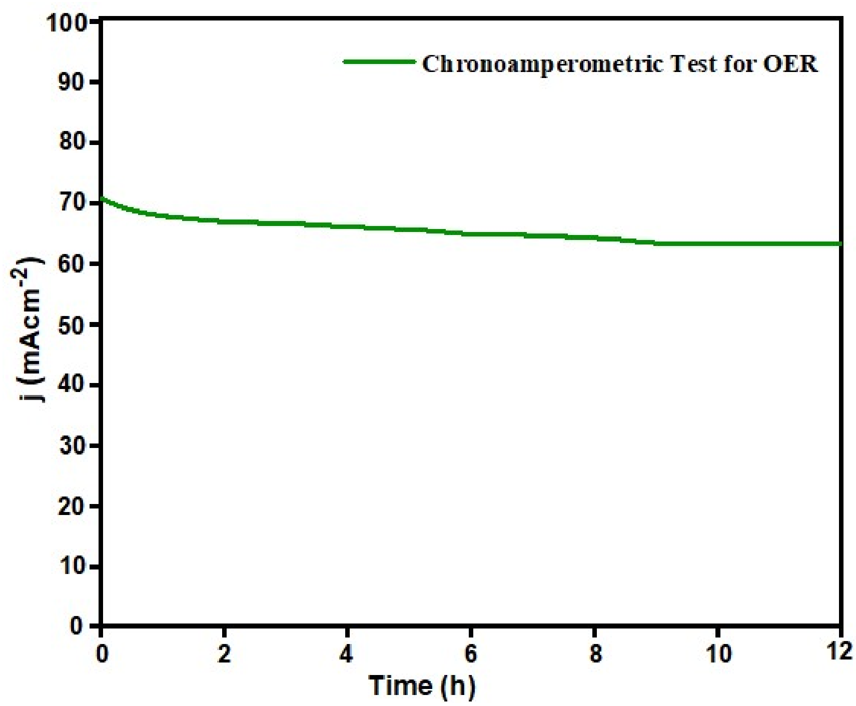


Figure S4. Chronoamperometric test for OER in 1 M KOH electrolyte

Table S1 C_{dl}, ECSA and R_f values of samples

Electrocatalyst	C_{dl} ($mFcm^{-2}$)	ECSA (cm^2)	R_f*
M1	0.33	16.5	235.7
M2	0.61	30.5	435.7
M3	1.15	57.5	821.4

Table S2 OER activities for various catalysts.

Name of the catalyst	Abbreviated name for catalyst	Overpotential (mV) at 10 mA/cm^2	Tafel value (mV/dec)	Mass activity @η=250 mV (A/g)	TOF @η=250 mV (sec^{-1})
MXene/MIL Fe-53/ZIF-67@50	M1	299	121	**13.9**	**0.38**
MXene/MIL Fe-53/ZIF-67@100	M2	271	73	**21.1**	**0.57**
MXene/MIL Fe-53/ZIF-67@200	M3	237	64	**57.5**	**1.56**

Table S3 HER activities for various catalysts.

Name of the catalyst	Abbreviated name for catalyst	HER overpotential (mV) at 10 mA/cm^2	Tafel value (mV/dec)	Mass activity @η=350 mV (A/g)	TOF @η=350 mV (sec^{-1})
MXene/MIL Fe-53/ZIF-67@50	M1	494	244	**6.4**	**0.35**
MXene/MIL Fe-53/ZIF-67@100	M2	369	205	**20**	**1.10**
MXene/MIL Fe-53/ZIF-67@200	M3	307	185	**54.6**	**2.97**

Table S4 Comparison of OER and HER overpotentials from reported literature

Catalyst	OER Overpotential at 10 mA/cm^2	HER Overpotential at 10 mA/cm^2	Ref.
Co-M-Fe/Ni(150)	269 mV	149 mV	[3]
CoP/NCNHP	1.64 V	140 mV	[4]
Co0.2Fe0.8Ni-OCNF	291 mV	259 mV	[5]
Co/NiMOFs@Fe	264 mV	------	[6]

References

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