Electronic Supplementary Information

Unidirectional Competitive Redox enabled Unsegmented Natural Sea-water Splitting for Green Hydrogen Production

Hemanga Pradhan,‡ Ritwik Mondal,‡ Bhojkumar Nayak,‡ Ravikumar Thimmappa, Rahul Mahadeo Mendhe, Musthafa Ottakam Thotiyl*

Department of Chemistry, Indian Institute of Science Education and Research, Pune, Dr. Homi Bhabha Road, Pune, 411008, India

*Correspondence: musthafa@iiserpune.ac.in

‡These authors contributed equally.

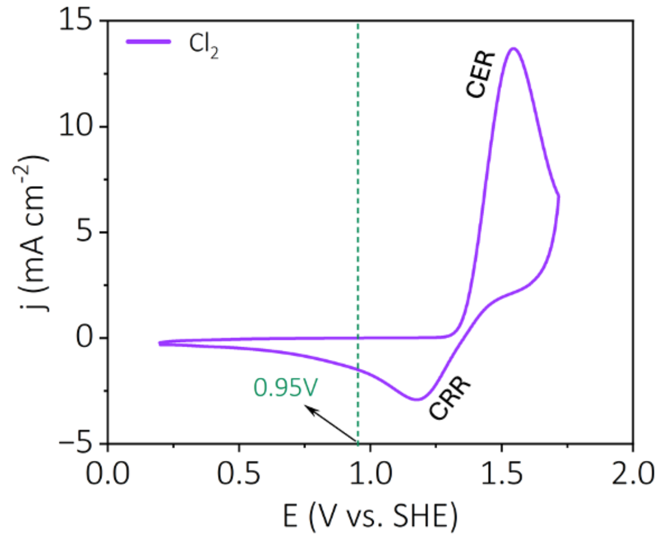


Fig. S1. Cyclic voltammogram demonstrating chlorine evolution reaction (CER) and chloride reduction reaction (CRR) occurring on a Pt electrode in argon-purged 0.6 M NaCl electrolyte at a scan rate of 20 mV/s.

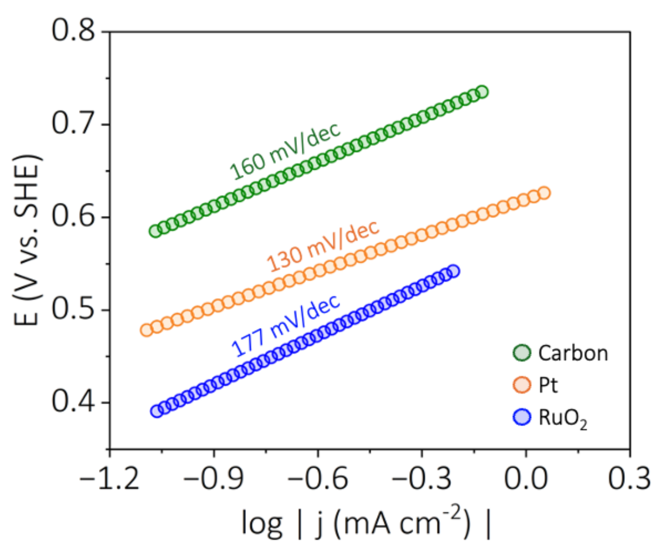


Fig. S2. Tafel plots for ascorbic acid oxidation with various electrocatalysts (extracted from Fig. 1c).

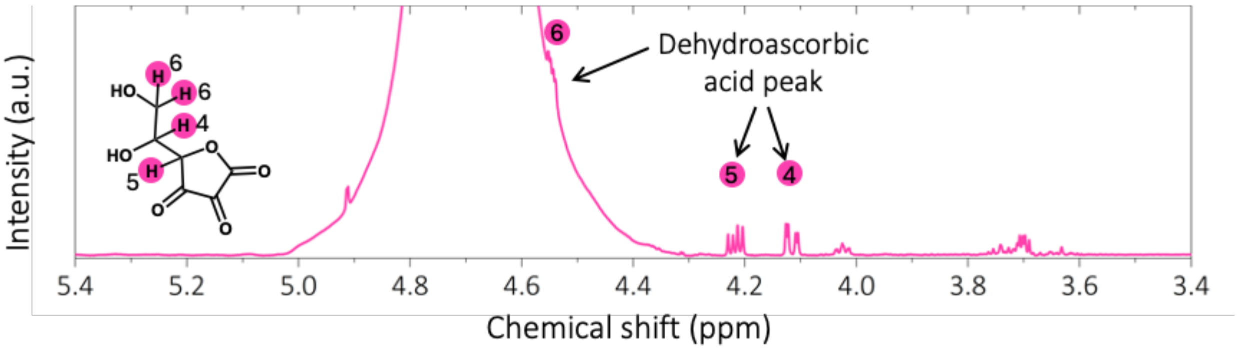


Fig. S3. ^{1}H NMR spectra of the electrolyte after electrolysis.

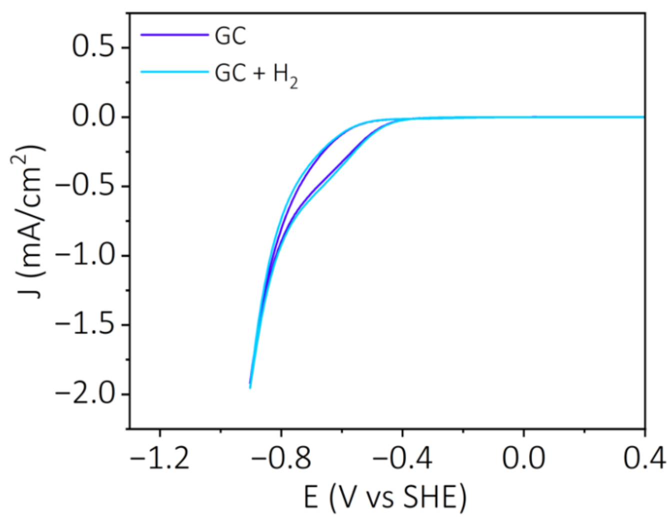


Fig. S4. Cyclic voltammograms of a hydrogen oxidation reaction in carbon electrode with and without purging H_2 in the electrolyte.

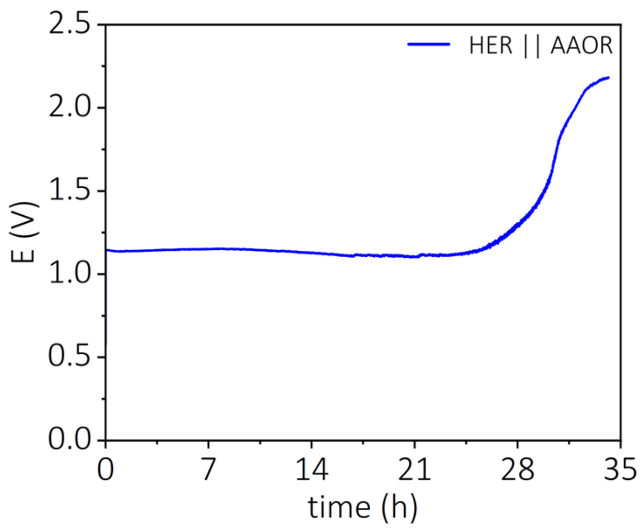


Fig. S5. Chronopotentiometry plots at 150 mA/cm^2 for the membraneless saline water electrolyzer, with and without AA in 0.6 M NaCl electrolyte. The anodic electrode is Ketjen black carbon (2 mg/cm^2), and the cathodic electrocatalyst is based on Pt/C (0.5 mg/cm^2).

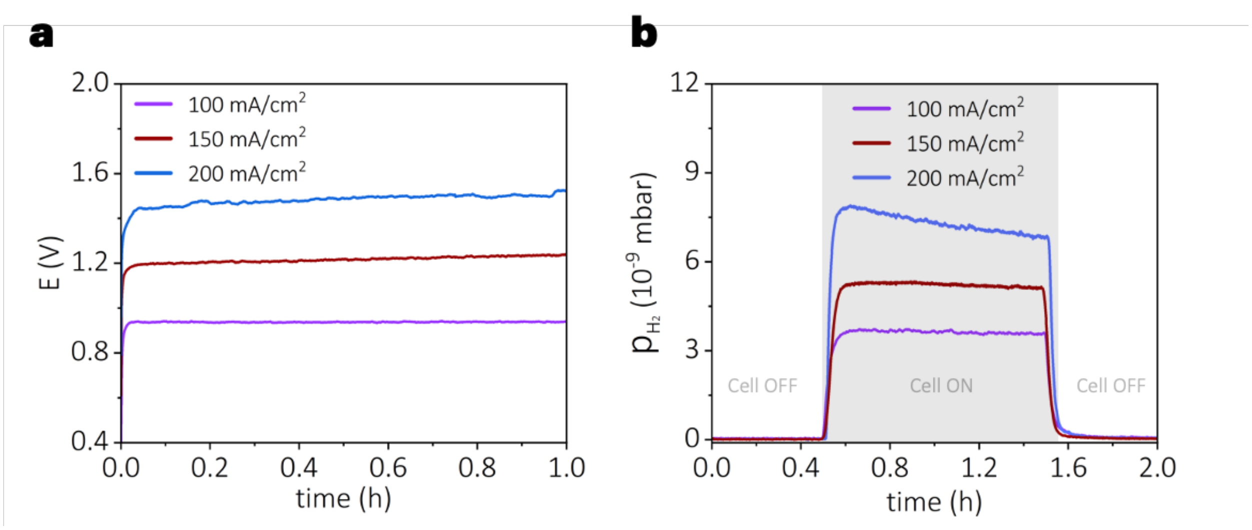


Fig. S6. (a) Rate capability study and (b) corresponding in-situ electrochemical mass spectra for membraneless saline water electrolyzer, with AA in 0.6 M NaCl electrolyte. The anodic electrode is Ketjen black carbon (2 mg/cm^2), and the cathodic electrocatalyst is based on Pt/C (0.5 mg/cm^2).

Calculation S1: Faradaic efficiency

For 100 mA/cm^2 : (Fig. S6a, purple trace)

Total charge passed for 1 h = 0.1 *3600 = 360 C

= 360/96485 = 0.00373 mol = 3.73 mmol

For the evolution of one H_2 molecule, it requires 2 electrons

So, the theoretical amount of H_2 evolved = 3.73/2 = 1.865 mmol

At room temperature (298K), 1 mole of H_2 gas is equivalent to 24.45 L of H_2

Therefore, the theoretical amount of H_2 gas evolved = (24.45* 1.865) mL = 45.599 mL

From the experiment, the amount of H_2 evolved = 43 mL

Faradaic efficiency = (43/45.599) * 100 = 94.30 %

For 150 mA/cm^2 : (Fig. S6a, brown trace)

Total charge passed for 1 h = 0.15 *3600 = 540 C

= 540/96485 = 0.00559 mol = 5.59 mmol

For the evolution of one H_2 molecule, it requires 2 electrons

So, the theoretical amount of H_2 evolved = 5.59/2 = 2.798 mmol

At room temperature (298K), 1 mole of H_2 gas is equivalent to 24.45 L of H_2

Therefore, the theoretical amount of H_2 gas evolved = (24.45* 2.798) mL = 68.419 mL

From the experiment, the amount of H_2 evolved = 63.5 mL

Faradaic efficiency = (63.5/68.419) * 100 = 92.82 %

For 200 mA/cm^2 : (Fig. S6a, blue trace)

Total charge passed for 1 h = 0.2 *3600 = 720 C

= 720/96485 = 0.00746 mol = 7.46 mmol

For the evolution of one H_2 molecule, it requires 2 electrons

So, the theoretical amount of H_2 evolved = 7.46/2 = 3.73 mmol

At room temperature (298K), 1 mole of H_2 gas is equivalent to 24.45 L of H_2

Therefore, the theoretical amount of H_2 gas evolved = (24.45* 3.73) mL = 91.198 mL

From the experiment, the amount of H_2 evolved = 84 mL

Faradaic efficiency = (84/91.198) * 100 = 92.11 %

Calculation S2: Total energy saved

Total energy saved = (energy required for HER||CER) – (energy required for HER||AAOR), which is equivalent to the shaded area between the chronopotentiometry traces in Fig. 4b.

= (96.6979 – 34.6601) V.h

= 62.0378 V.h

Energy saved = Shaded area * Current

= 62.0378 * 150 * 10^{-3}* 3600 V.A.s

= 33,500 J = 33.5 kJ

Total moles of AA consumed = 0.0849 mol

The amount of energy saved per mole = 33.5/0.0849 kJ mol^{-1}

= 394.6 kJ mol^{-1}

Energy savings in percentage = Energy saved / Energy required for HER||CER

= 64.16 %

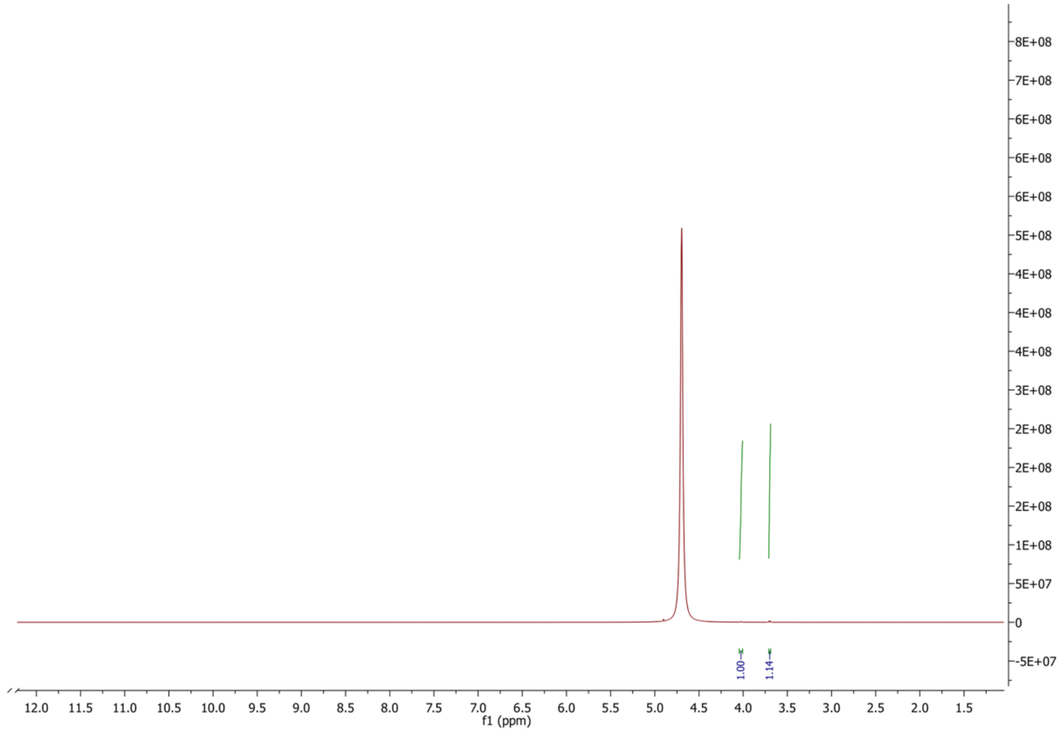


Fig. S7. Full range ^{1}H NMR spectra of the electrolyte before electrolysis

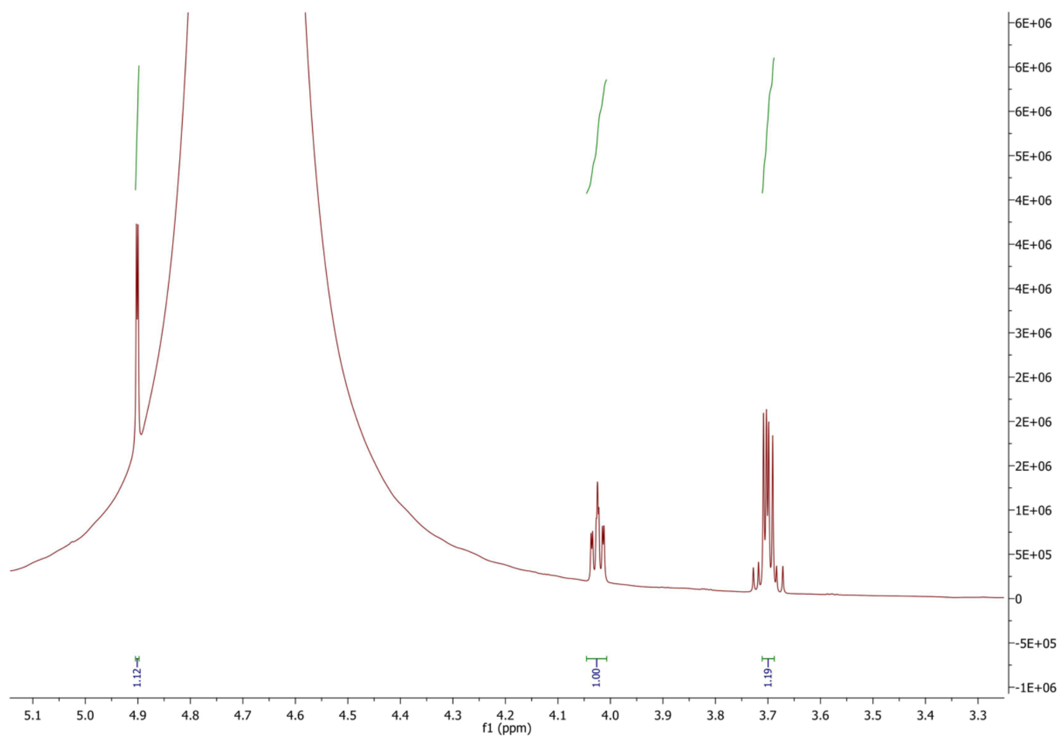


Fig. S8. Zoomed view of ^{1}H NMR spectra of the electrolyte before electrolysis.

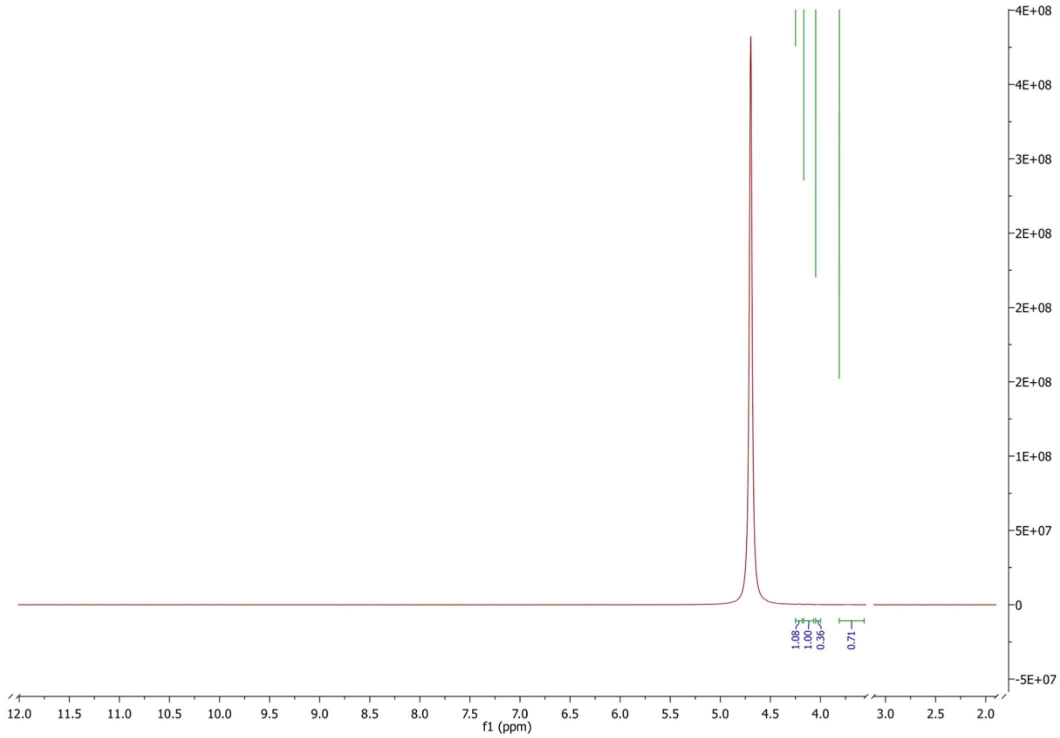


Fig. S9. Full range ^{1}H NMR spectra of the electrolyte after electrolysis.

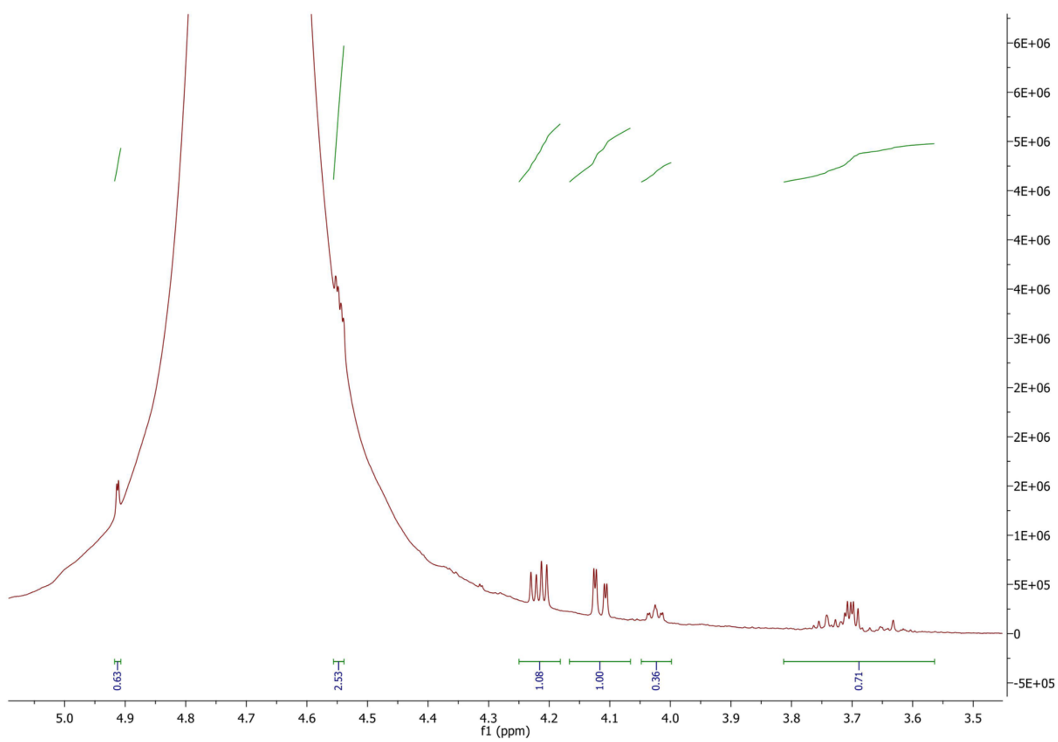


Fig. S10. Zoomed view of ^{1}H NMR spectra of the electrolyte after electrolysis.

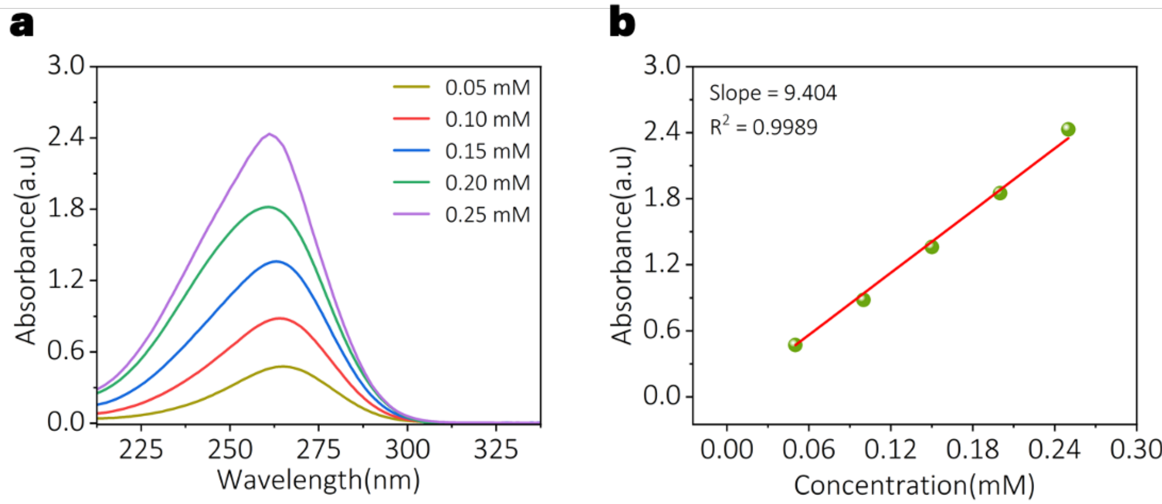


Fig. S11. (a) UV-Vis absorption spectra for ascorbic acid with various concentrations. (b) Linear fit between absorbance and concentration of ascorbic acid (AA).

Calculation S3: Charge balance

The initial concentration of AA = 1 M

From the calibration plot (Fig. S11b), the slope = 9.404

For UV visible spectra, we diluted the solution 4000 times

After 30h, the absorbance of AA = 0.355

The concentration after 30 h = 0.355/9.404 = 0.0377*4000

= 150.999 mM

Volume = 100 mL

Amount of AA after 30 h = 15.099 mmol

So, the number of moles of AA consumed during 30 h = 100 – 15.099 = 84.901 mmol

= 0.0849 mol

The charge passed at a constant current of 150 mA for 30 h = 0.15 * 3600 * 30

= 16200 C

= 0.1674 mol

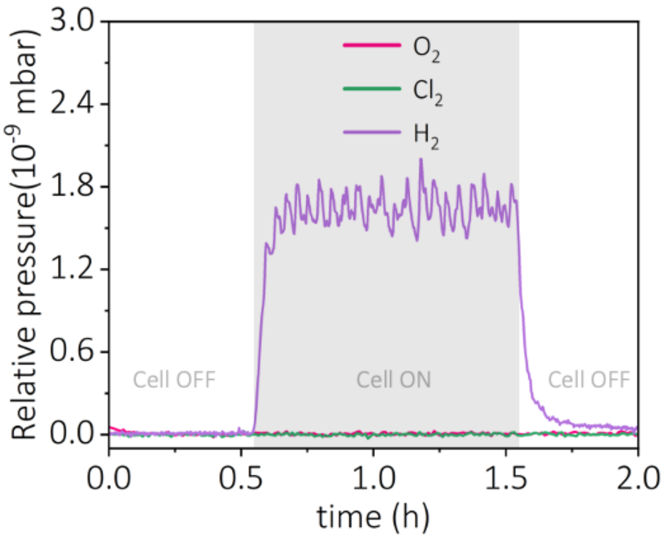


Fig. S12. In situ electrochemical mass spectrum for O_2 and Cl_2 detection during the constant current test at 50 mA/cm^2 for hydrogen production in an undivided cell.

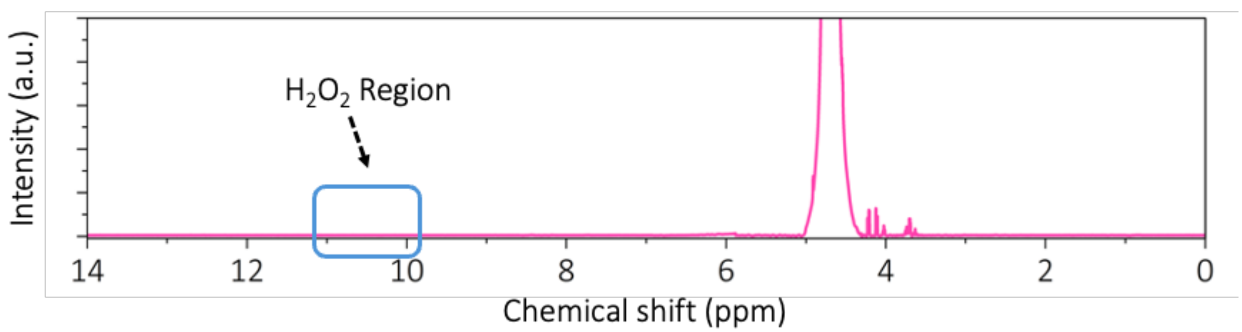


Fig. S13. ^{1}H NMR spectra of the electrolyte after long-term electrolysis.

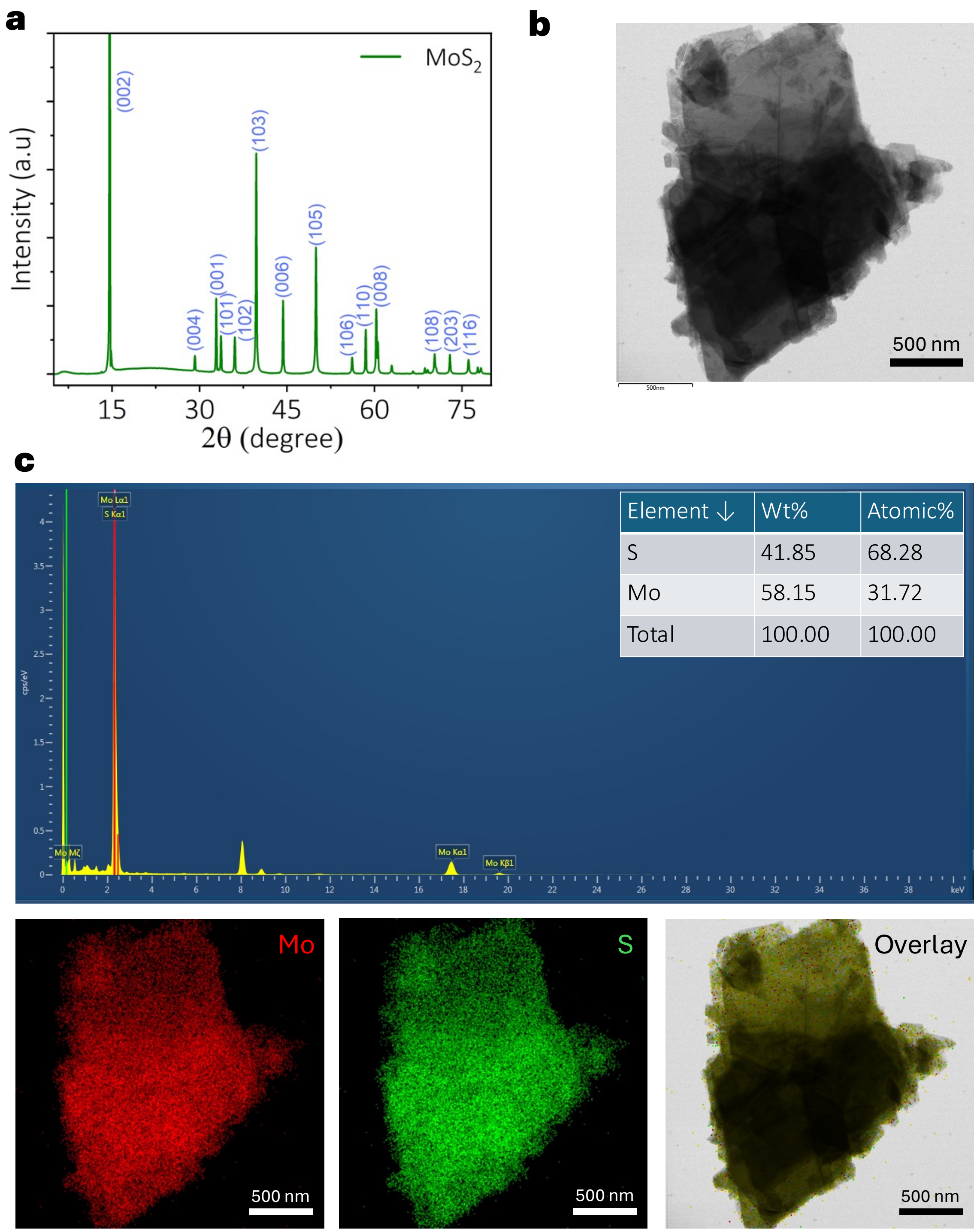


Fig. S14. (a) XRD pattern for MoS_2 corresponds to JCPDS: 00-037-1492. (b) TEM image and (c) EDX spectrum and the corresponding elemental mapping images for Mo and S in MoS_2.

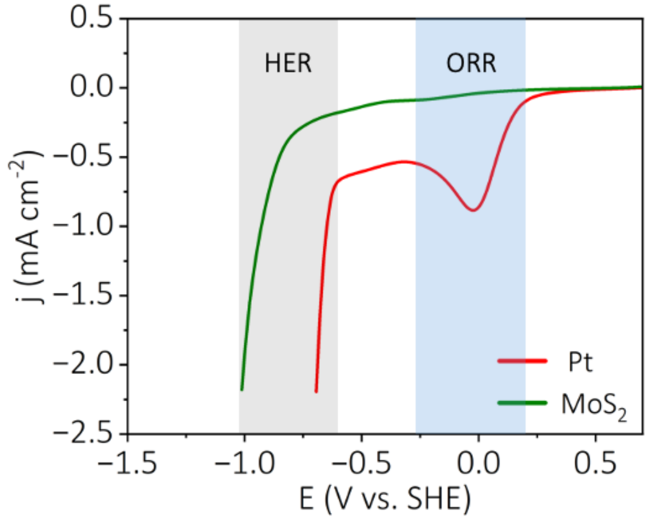


Fig. S15. (a) Linear sweep voltammograms for Pt and MoS_2 electrocatalysts at a scan rate of 20 mV/s in the presence of dissolved oxygen.

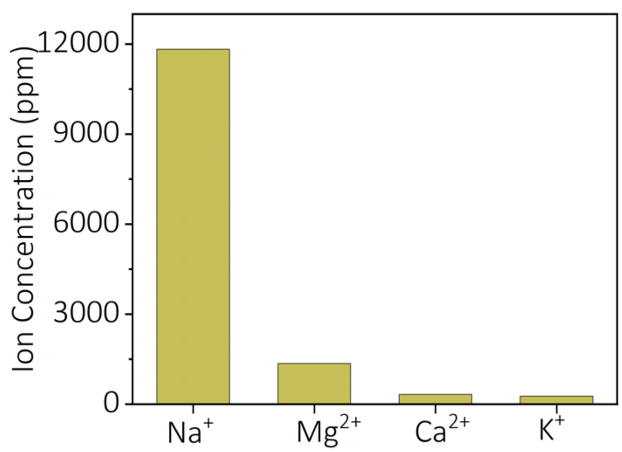


Fig. S16. MP-AES elemental analysis of natural seawater obtained from the Bay of Bengal (Chennai coastal area, India).

Calculation S4: Hydrogen quantification (from Fig. 6f)

At a constant current of 50 mA/cm^2

For 1 h

Total charge passed for 1 h = 0.05 *3600 = 180 C

= 180/96485 = 0.001865 mol = 1.865 mmol

For the evolution of one H_2 molecule, it requires 2 electrons

So, the theoretical amount of H_2 evolved = 1.865/2 = 0.932 mmol

At room temperature (298K), 1 mole of H_2 gas is equivalent to 24.45 L of H_2

Therefore, the theoretical amount of H_2 gas evolved = (24.45* 0.932) mL = 22.787 mL

From the experiment, the amount of H_2 evolved = 22 mL

Faradaic efficiency = (22/22.787) * 100 = 96.54 %

For 2 h

Total charge passed for 2 h = 0.05 *7200 = 360 C

= 360/96485 = 0.00373 mol = 3.73 mmol

For the evolution of one H_2 molecule, it requires 2 electrons

So, the theoretical amount of H_2 evolved = 3.73/2 = 1.865 mmol

At room temperature (298K), 1 mole of H_2 gas is equivalent to 24.45 L of H_2

Therefore, the theoretical amount of H_2 gas evolved = (24.45* 1.865) mL = 45.599 mL

From the experiment, the amount of H_2 evolved = 43.5 mL

Faradaic efficiency = (43.5/45.599) * 100 = 95.40 %

For 3 h

Total charge passed for 3 h = 0.05 *10800 = 540 C

= 540/96485 = 0.005596 mol = 5.596 mmol

For the evolution of one H_2 molecule, it requires 2 electrons

So, the theoretical amount of H_2 evolved = 5.596/2 = 2.798 mmol

At room temperature (298K), 1 mole of H_2 gas is equivalent to 24.45 L of H_2

Therefore, the theoretical amount of H_2 gas evolved = (24.45* 2.798) mL = 68.42 mL

From the experiment, the amount of H_2 evolved = 65 mL

Faradaic efficiency = (65/68.42) * 100 = 95.00 %

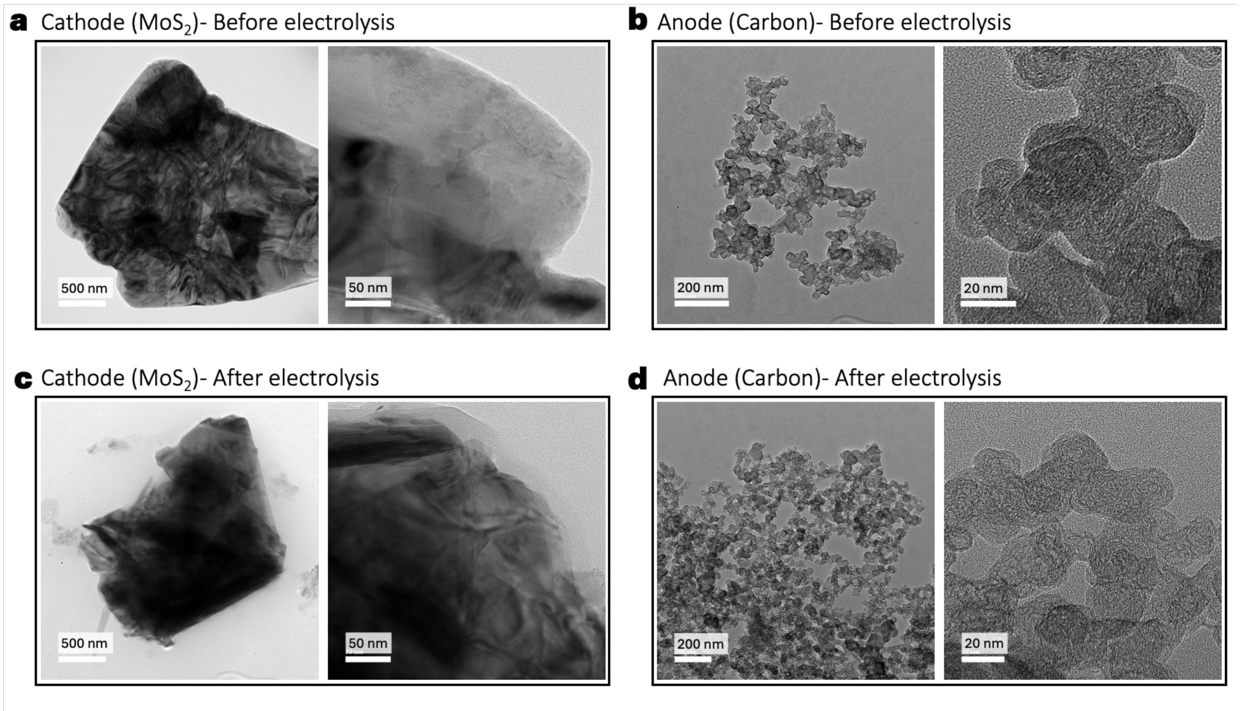


Fig. S17. TEM images of (a) cathode electrocatalyst-before electrolysis, (b) anode electrocatalyst-before electrolysis, (c) cathode electrocatalyst-after electrolysis, and (d) anode electrocatalyst-after electrolysis.

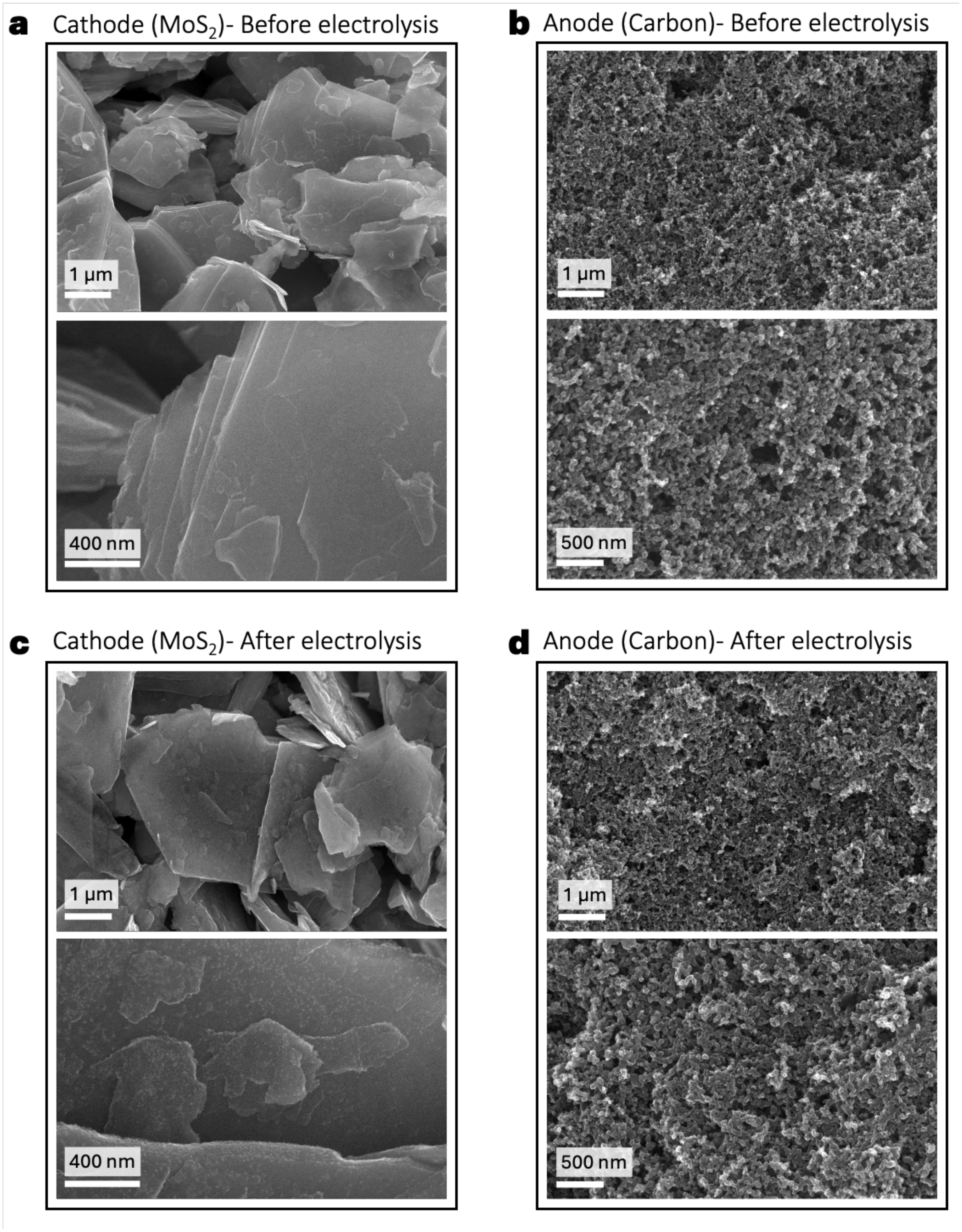
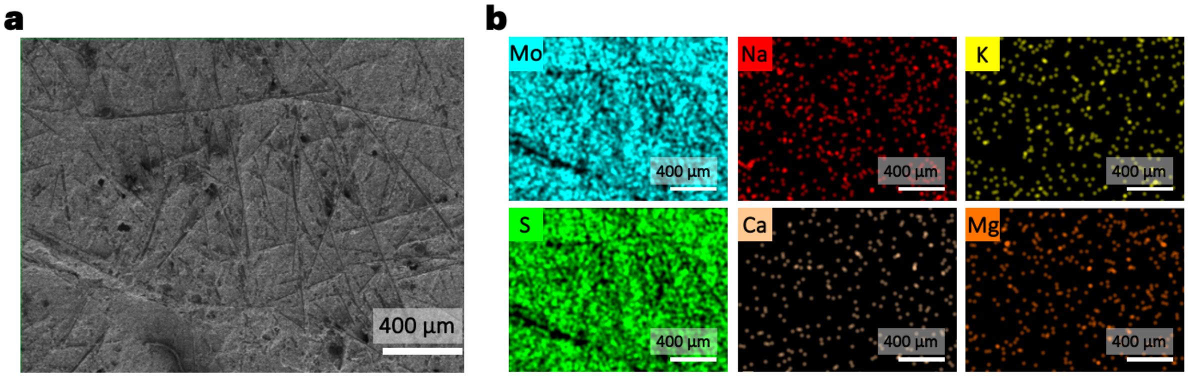
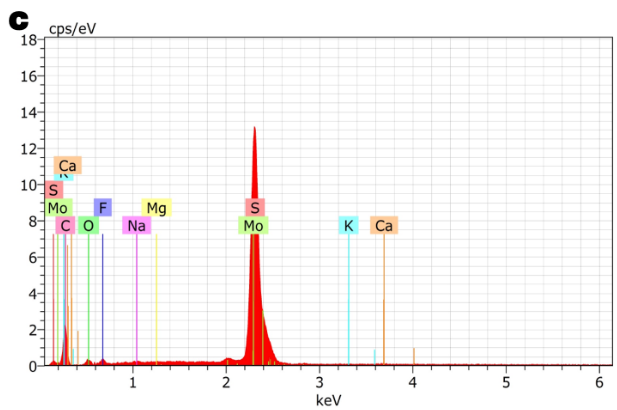


Fig. S18. SEM images of (a) cathode electrocatalyst-before electrolysis, (b) anode electrocatalyst-before electrolysis, (c) cathode electrocatalyst-after electrolysis, and (d) anode electrocatalyst-after electrolysis.





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Element	AN	series	Unn. C (wt.%)	Norm. C (wt.%)	C Atom (at.%)	C error(1 sigma) (wt%)
C	6	K	24.02	37.39	67.88	4.06
Mo	42	L	20.34	31.66	7.2	0.75
S	16	K	14.29	22.24	15.12	0.54
O	8	K	2.82	4.39	5.98	0.74
F	9	K	1.45	2.26	2.6	0.4
K	19	K	1.12	1.74	0.97	0.11
Na	11	K	0.08	0.12	0.11	0.04
Mg	12	K	0.07	0.11	0.1	0.04
Ca	20	K	0.06	0.09	0.05	0.03
			64.25	100	100	

Fig. S19. (a) SEM image of MoS_2 electrode after long-term electrolysis with (b) the elemental mapping images for different ions. (c) EDX spectrum and (d) elemental composition table (Fluorine in the table is derived from the Nafion binder).

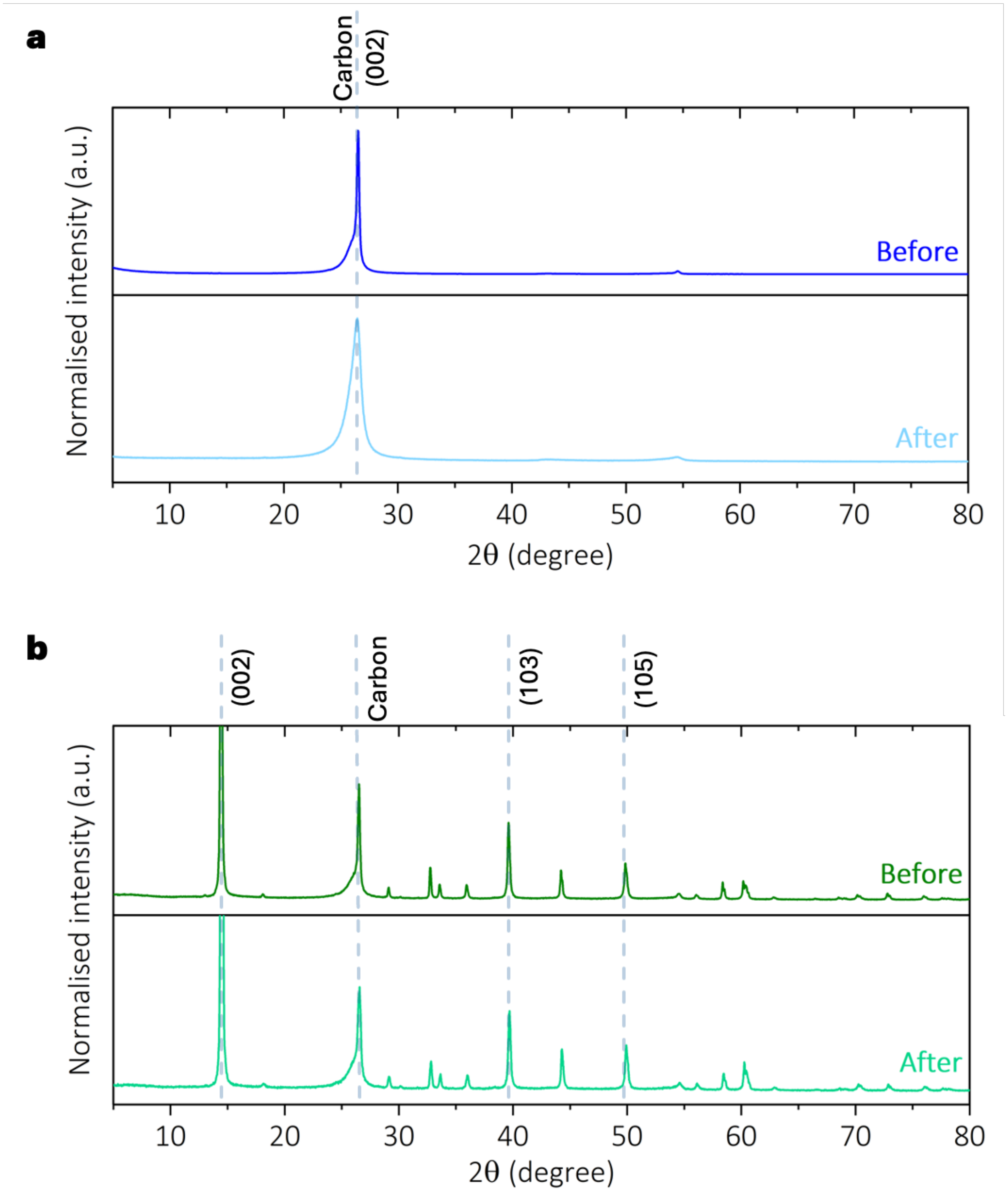

Fig. S20. XRD spectra of (a) Anode (carbon) electrocatalyst before and after electrolysis, (b) Cathode (MoS_2) electrocatalyst before and after electrolysis.

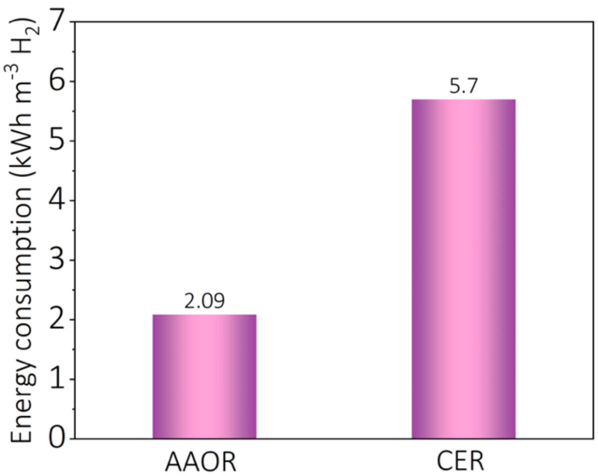

Fig. S21. Comparisons of energy consumption, with and without ascorbic acid (Corresponds to Fig. 4a).

Calculation S5: Energy consumption (from Fig. 4a)

With Ascorbic acid

The required voltage to maintain a current of 100 mA/cm^2 = 0.9 V

Energy consumption = 0.9 * 0.1* 1 Wh

= 0.09 Wh

Amount of H_2 production = 43 mL

Energy consumption = 0.09/43*10^{-6} Wh.m^{-3}

= 2.09 kWh m^{-3}

Without Ascorbic acid

The required voltage to maintain a current density of 100 mA/cm^2 = 2.45 V

Energy consumption = 2.45 * 0.1* 1 Wh

= 0.245 Wh

Amount of H_2 production = 43 mL

Energy consumption = 0.245/43*10^{-6} Wh.m^{-3}

= 5.7 kWh m^{-3}

Total energy saved during electrolysis = (5.7 – 2.09) kWh m^{-3}

= 3.61 kWh m^{-3}

Table S1: Comparison of unsegmented natural seawater electrolyzer system with previously reported water splitting systems.

Serial no.	Anodic Reaction	Electrolyte	Cell voltage at 100 mA/cm^2 (V)	Energy consumption (kWh/m^3 H_2)	Reference
1	Ascorbic acid oxidation	Ascorbic acid + Seawater (+, –)	0.90	2.09	This work
2	Oxygen evolution reaction	Seawater (+, –)	2.45	5.7	This work
3	Sulphur Oxidation reaction	1.0 M NaOH + 2.0 M Na2S (+) || H2O || 2.5 M H2SO4 (-)	1.32	3.16	*Angew. Chemie Int. Ed.*, 2021, **60**, 21550–21557
4	Hydrazine oxidation reaction	1.0 M KOH + 0.1.0 M N_2H_4 (+, –)	0.61	1.46	*Sci. Adv.*, 2020, **6**, eabb4197
5	Methanol Oxidation reaction	2.0 M MeOH + 1.0 M NaOH + 3.5% NaCl (+, –)	1.08	2.58	*J. Mater. Chem. A*, 2021, **9**, 6316–6324
6	Urea Oxidation reaction	1.0 M KOH+ 0.5 M urea (+, –)	1.395	3.34	*Carbon Energy*, 2023, **5**, 1–13
7	Glucose oxidation Reaction	1.0 M KOH + 0.5 M glucose (+) || 1.0 M KOH (–)	1.39	3.33	*Nat. Commun.*, 2020, **11**, 1–11
8	HMF oxidation reaction	1.0 M KOH + 1.0 M HMF (+) || 1.0 M KOH (–)	1.70	4.07	*Adv. Mater.*, 2020, **32**, 1–10
9	Benzyl alcohol Oxidation Reaction	1.0 M KOH + 0.5 M benzyl alcohol (+) || 1.0 M KOH (–)	1.82	4.37	*Adv. Funct. Mater.*, 2017, **27**, 1–11
10	Oxygen Evolution Reaction	1.0 M KOH seawater	1.8	4.31	*Adv. Funct. Mater.*, 2021, **31**, 1–12