In-situ Pd doped MoS_2 nanosheets as HER electrocatalyst for enhanced electrocatalytic water splitting

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Supplementary information

Table SI1: Details of added amount (mg) of palladium chloride precursor for Pd doping in MoS_2, their respective sample name and synthesis parameters.

Sample Name	Added weight of Pd precursor (mg)	Reaction temperature (^{0}C)	Reaction time (hours)
Pd-MS1	5	180	24
Pd-MS2	10	180	24
Pd-MS3	20	180	24
Pd-MS4	30	180	24
Pd-MS5	40	180	24
Pd-MS6	50	180	24

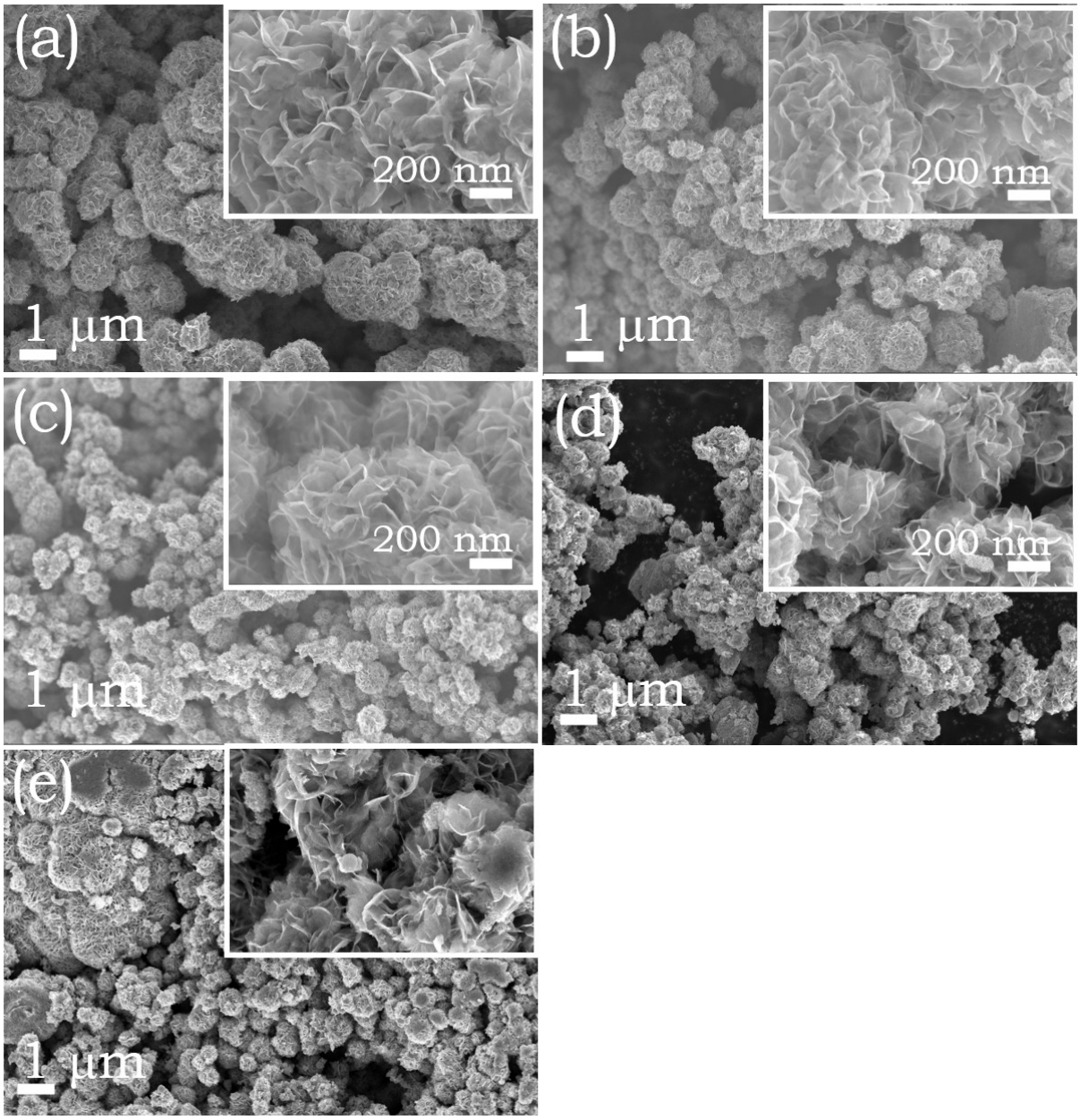

Figure SI1: FESEM images of (a) Pd-MS1, (b) Pd-MS2, (c) Pd-MS3, (d) Pd-MS4 and (e) Pd-MS6.

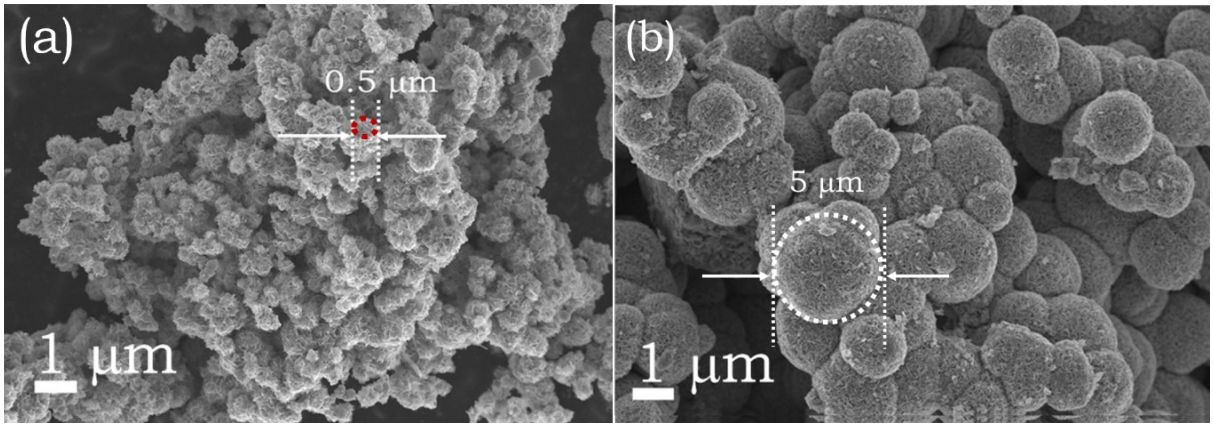

Figure SI2: Dimension of micro balls in FESEM images of (a) Pd-MS5 and (b) pristine MoS_2.

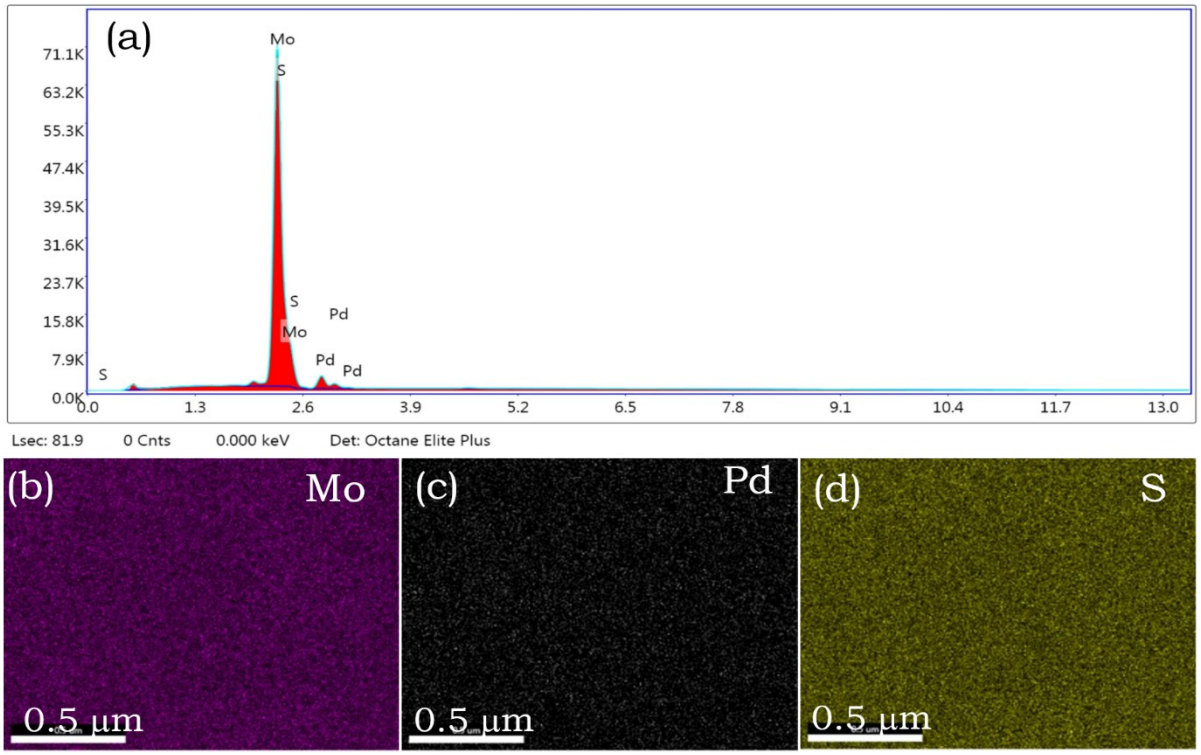

Figure SI3: (a) EDAX pattern and (b, c, & d) area mapping for element Mo, Pd and S respectively p resent in sample Pd-MS5.

Table SI2: EDS report for hydrothermally synthesized Pd-MoS_2 and pristine MoS_2 powders.

Sample	**Mo (At%)**	**S (At %)**	**Pd (At %)**
Pristine MoS_2	31.09	68.91	-
Pd-MS1	30.95	68.66	0.4
Pd-MS2	31.77	66.61	1.61
Pd-MS3	29.13	68.22	2.65
Pd-MS4	29.22	66.79	3.99
Pd-MS5	26.16	67.59	5.25
Pd-MS6	28.78	64.89	6.33

Estimation of ESCA of Electrode –

Electrochemical Surface Area (ESCA) of electrode is proportional to its double layer capacitance (C_{dl}), which was calculated by cyclic voltammetry (CV) study at different scan rates of 10, 20, 30, 40, 50 ,60, 70, 80, 90, 100 mV.sec^{-1} within the non – Faradic region of the electrode. Figure SI4 shows the recorded CV curve with scan rates in acidic (a), alkaline (b), and simulated sea water (c) for the sample Pd-MoS_2.

The C_{dl} was estimated by observing the difference of anodic & cathodic current density at 0.1 V *vs.* SCE with respect to the scan rate.

$$C_{dl} = \frac{d(\Delta J)}{dV_b} \qquad ..eq.\ (i)$$

Where V_b is the scan rate.

The ECSA was calculated from the c_{dl} using the following relation –

$$ECSA = \frac{C_{dl}}{C_s} \qquad ..eq.\ (ii)$$

Where, C_s is the specific capacitance of flat smoot surface with 1 cm^2 of real surface area which is consider 60 µF for MoS_2 and doped MoS_2 system whereas it is 20 µF for sample Pt/C [1] .

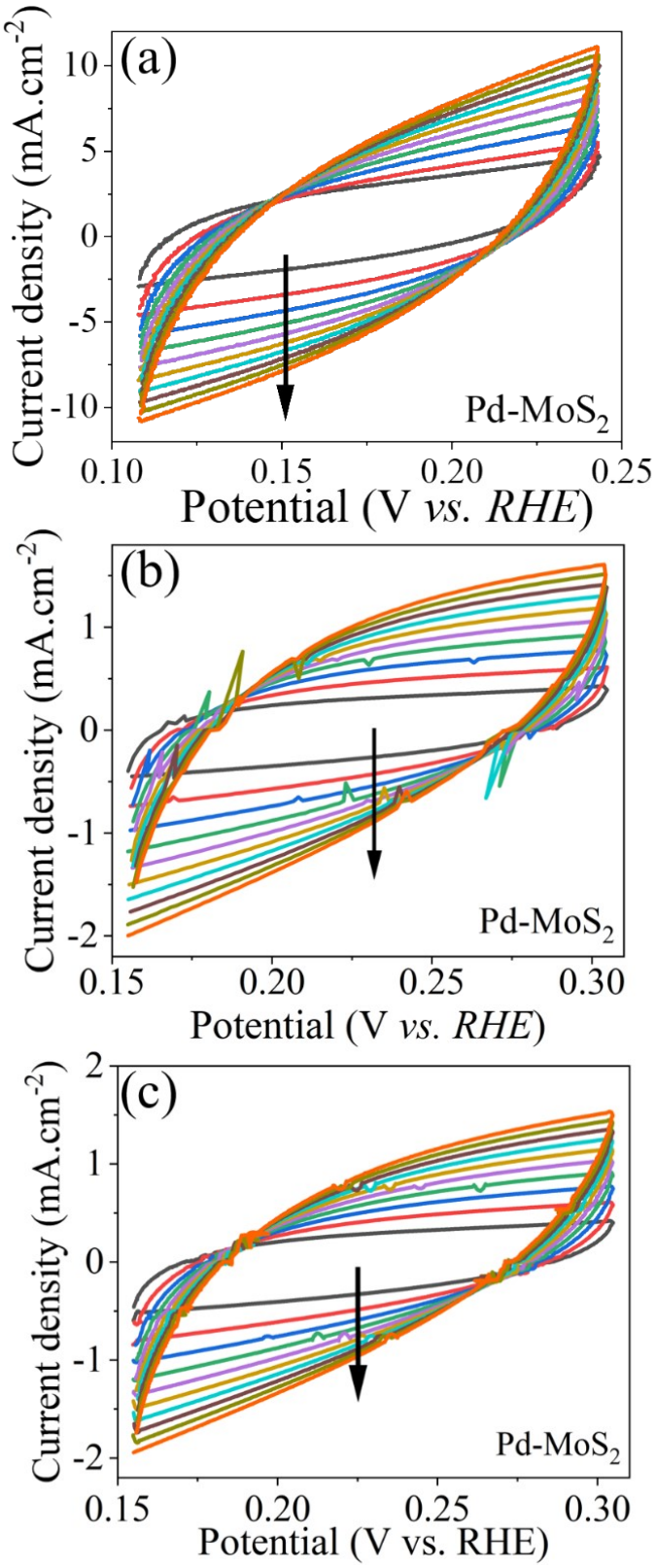

Figure SI4: CV curves recorded at different scan rates in (a) acidic, (b) alkaline, and (c) simulated sea water to calculate the ECSA for the sample Pd-MoS_2.

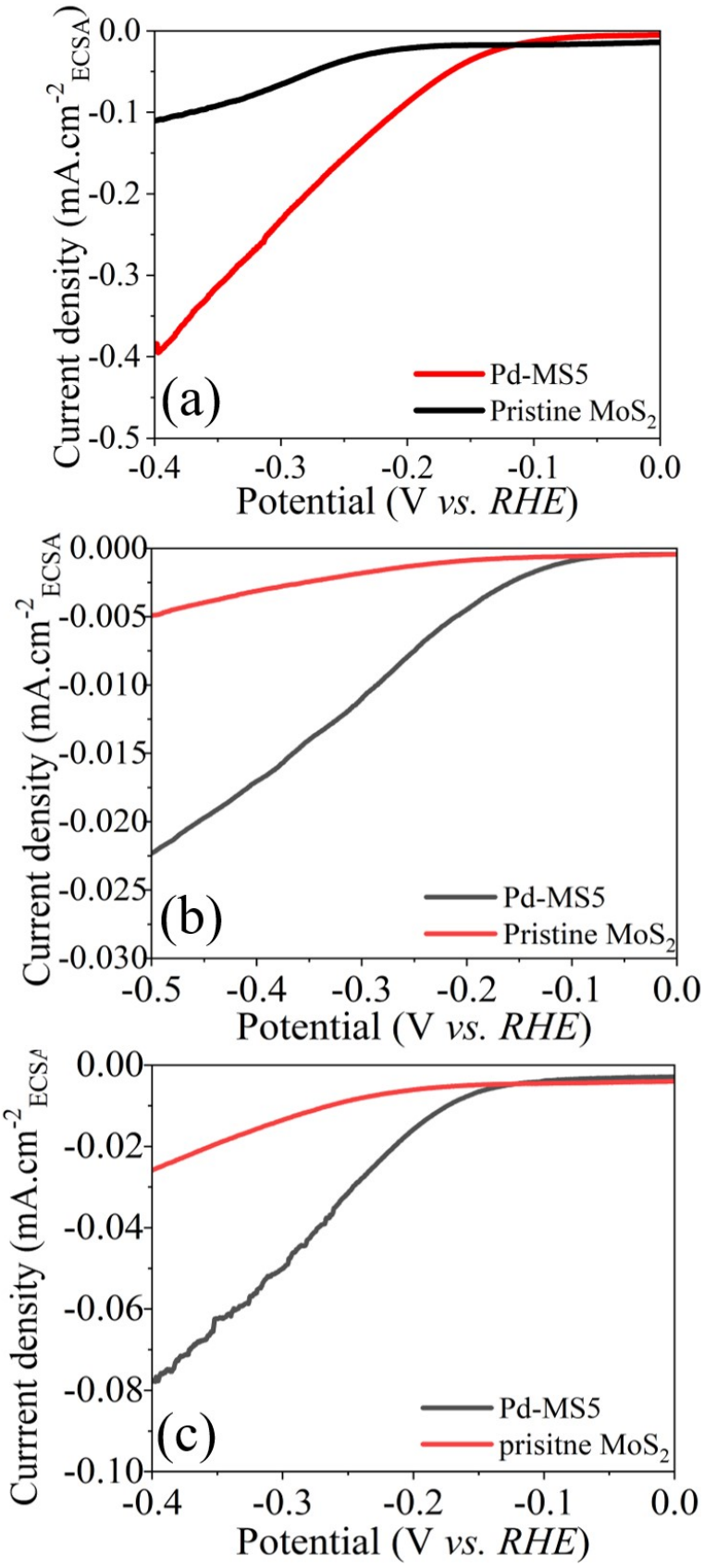

Figure SI5: The ECSA-normalized polarization activity of pristine MoS_2 and Pd doped MoS_2 (Pd-MS5: optimized) for HER application in (a) acidic condition (b) alkaline condition and (c) simulated seawater condition.

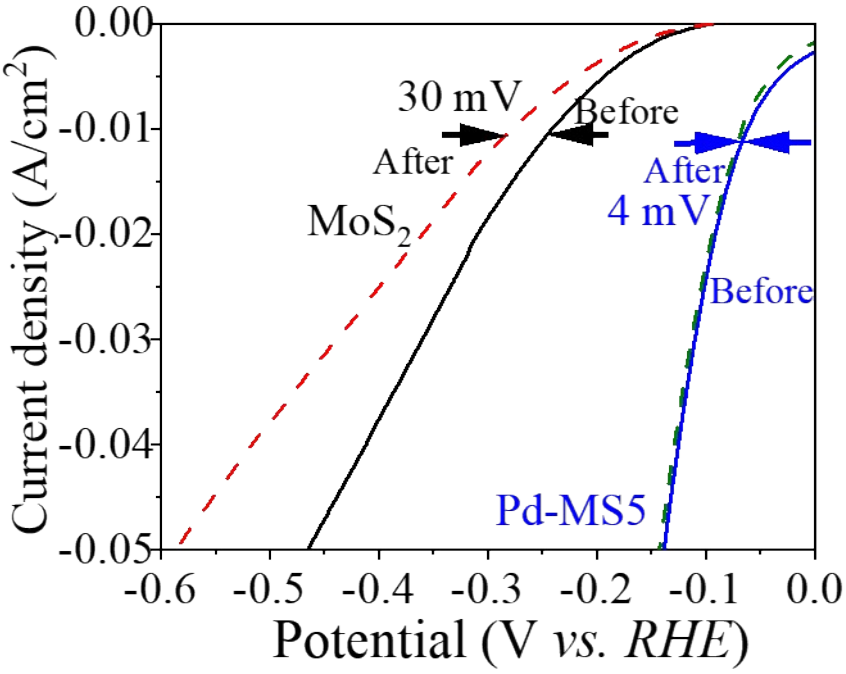

Figure SI6: The polarization curve recorded before and after 1000 CV cycles for the samples Pd-MoS_2 (Pd-MS5) and pristine MoS_2.

Table SI3: Quantification of evolved H_2 and O_2 gases from system Pd-MoS_2\|\|C.P. and MoS_2\|\|C.P. during electrocatalytic water splitting in acidic, alkaline, and simulated sea water.

Electrolyte	**Time (min)**	**H_2 (µmol)**		**O_2 (µmol)**	
		Pd-MoS_2||C.P.	**MoS_2||C.P.**	**Pd-MoS_2||C.P.**	**MoS_2||C.P.**
Acidic (0.5 M H_2SO_4)	15	221.86	104.93	101.98	48.95
	30	381.52	173.76	156.24	75.12
	45	495.90	235.96	214.98	105.49
	60	641.09	307.54	264.26	131.13
	75	740.8	350.19	291.97	143.99
Alkaline (1M KOH)	15	158.22	40.12	79.10	15.06
	30	268.70	67.09	120.35	30.54
	45	496.61	114.42	225.40	52.21
	60	534.08	134.65	253.04	65.32
	75	622.10	155.77	297.05	71.88

Simulated sea water (1M KOH+0.5M NaCl)	15	138.84	20.97	64.45	9.48
	30	177.97	53.61	85.99	22.83
	45	287.02	97.66	140.51	43.83
	60	362.07	116.06	179.04	55.03
	75	403.23	149.47	201.02	71.73

Table SI4: HER Performance of various transition metal based electrocatalysts.

System	**Electrolyte**	**HER performance**	**Ref.**
Co_4Mo_2@NC	Alkaline water	218 mV@ 10 mA.cm^{-2}	[2]
Pd-MoS_2/RGO	Alkaline water	86 mV@ 10 mA.cm^{-2}	[3]
Mn–NiO–Ni/Ni–F	Seawater	170 mV@ 10 mA.cm^{-2}	[4]
NiCoN|NixP|NiCoN	Seawater	165 mV@ 10 mA.cm^{-2}	[5]
lepidocrocite VOOH	Alkaline water	164 mV@ 10 mA.cm^{-2}	[6]
PtRuMo	Seawater	196 mV@ 10 mA.cm^{-2}	[7]
NiFe–PBA–gel–cal	Alkaline simulated seawater	480 mV @ 100 mA.cm^{-2}	[8]
Co10%–VS_2	Simulated seawater	576 mV @ 100 mA.cm^{-2}	[9]
Fe–Co_2P BNRs	Seawater	489 mV @10 mA.cm^{-2}	[10]
Au–Gd–Co_2B@TiO_2	Alkaline seawater	194 mV @ 500 mA.cm^{-2}	[11]
Co–Fe_2P	Alkaline simulated seawater	221 mV @100 mA.cm^{-2}	[12]
N doped Ni_2S_3	Alkaline water	155 mV @10 mA.cm^{-2}	[13]
MoS_2 QD-aerogel-100	Seawater	380 mV @ 10 mA.cm^{-2}	[14]
NP–MoS_2/CC	Alkaline seawater	345 mV @10 mA.cm^{-2}	[15]
Ni-Co LDH/Co_9S_8	Alkaline water	142 mV @10 mA.cm^{-2}	[16]
NiCoP/NiCo–LDH@NF	Alkaline simulated seawater	213 mV @ 50 mA.cm^{-2}	[17]
RuV–CoNiP/NF	Alkaline seawater	81 mV @ 50 mA.cm^{-2}	[18]
PtRuNi	Seawater	206 mV @ 10 mA.cm^{-2}	[7]

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