Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Preparation of Bifunctional Ultrathin Nickel Phosphide Nanosheet Electrocatalyst for Full Water Splitting

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Experimental Section

All chemicals are used without any further purification.

Synthesis of $Ni(OH)_2$ Nanosheet Precursor

$Ni(OH)_2$ ultrathin freestanding nanosheets had grown by a facetious microwave-assisted technique conferring our past study[1]. In a distinctive process, 15 mmol of $Ni(NO_3)_2.6H_2O$ and 60 mmol urea (CH_4N_2O) had beenliquefied in 240 mL synthesis solvent of DI water (deionized water) and E.G (ethyleneglycol) with volume ratio 1:7 for 0.5 h to form a rich olive green uniform solution. The solution was formerly poured into a 1000 mL three-neck flask and put in the microwave treatment in a SINEOMAS-II+ microwave reactor at 700 W for 30 minutes in continuous stirring. Lastly, a fluffy olive green colloid precipitous had acquired, cooled it at room temperature recovered through centrifugation and wash away various times by DI water and ethanol.

Synthesis of Nickel Phosphide Ni_2P Ultrathin Freestanding Nanosheets

Ni_2P were prepared through chemical vapor deposition (CVD) method by using above fabricated nickel hydroxide $Ni(OH)_2$ and sodium hypophosphite (NaH_2PO_2) with a molar ratio (1:5). In a typical preparation of Ni_2P, both reactants were placed in a reactant tube in two different boats for 25 minutes and removed other gases with Ar flow. Then the precursors were heated at a temperature of 350°C through a temperature ramp of 1 °C/min and sustained on the final temperature for 180 min under Ar flow. Later cooled at room temperature and collected the black product.

Material Characterization

X-ray diffractometry (PANalytical XRD, with Cu Ka radiation) was used for the investigation of crystallographic phase. Microstructures and morphology of samples were observed via field emission scanning electron microscopy (FESEM, JEOL JEM-2100 F) fortified with energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM, JSM- 2100F, 200 kV), and high-resolution TEM (HRTEM, FEI Tecnai G2 F20, 200 kV). Using Veeco instrument atomic force microscopy (AFM) had been performed. Brunauer-Emmett-Teller surface areas (BET) was used for investigation of the specific surface area. PHI Quanteral II (Japan) with an Al K= 280.00 eV excitation source was used for the measurements of X-ray photoelectron spectroscopy (XPS).

Electrochemical Measurements

Electrochemical work station (CHI-660E) was used for all HER and OER in a three electrode system. Two electrode systems are used for overall water splitting, and saturated calomel (SCE) and Pt foil were taken as counter and reference electrodes for electrochemical measurements. Now a distinctive making of working electrode, a glassy carbon electrode (GCE) was used, 14 mg of Ni_2P was uniformly dissolved in water/ethanol solution (1/0.880 ml) and put it on sonication for 30 minutes, 940 µl of the stock solution and 60 µl of Nafion solution (Sigma Aldrich, 5wt%) were homogeneously mixed and sonicated for 30 min. Then, catalytic electrodes were fabricated by wise dropped 5 µl of the slurry on glassy carbon electrode (GCE) and dried it at room temperature.

Reversible Hydrogen Electrode used as a standard for all potentials as follows:

$$E(RHE) = E(SCE) + 0.059\ pH + Eo$$

Overall water electrolyzer has been prepared with 7 µl of the ink was loaded on 0.05 cm × 1 cm active area of carbon fiber paper electrode, before testing dried it at room temperature.

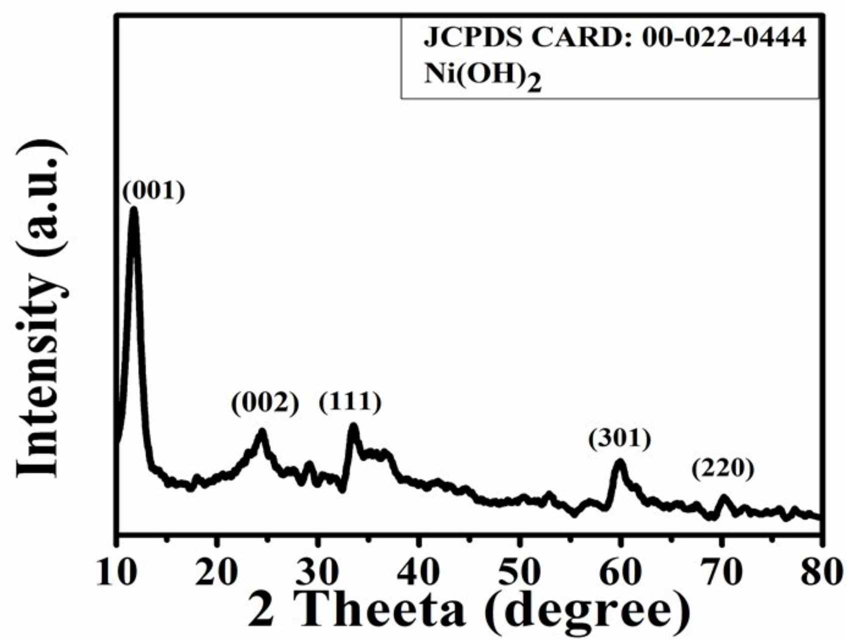

Figure S1. XRD pattern of Ni $(OH)_2$

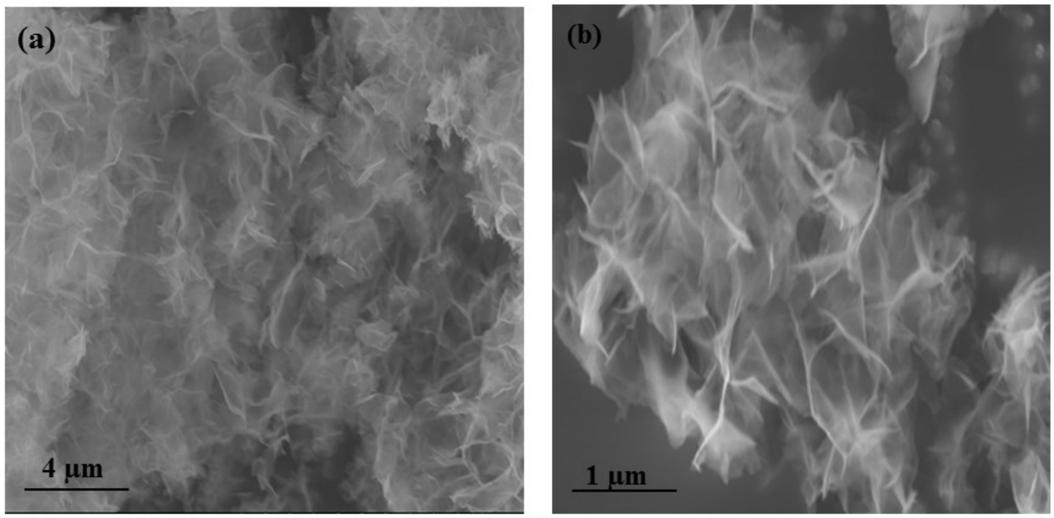

Figure S2. (a&b) SEM images of Ni $(OH)_2$

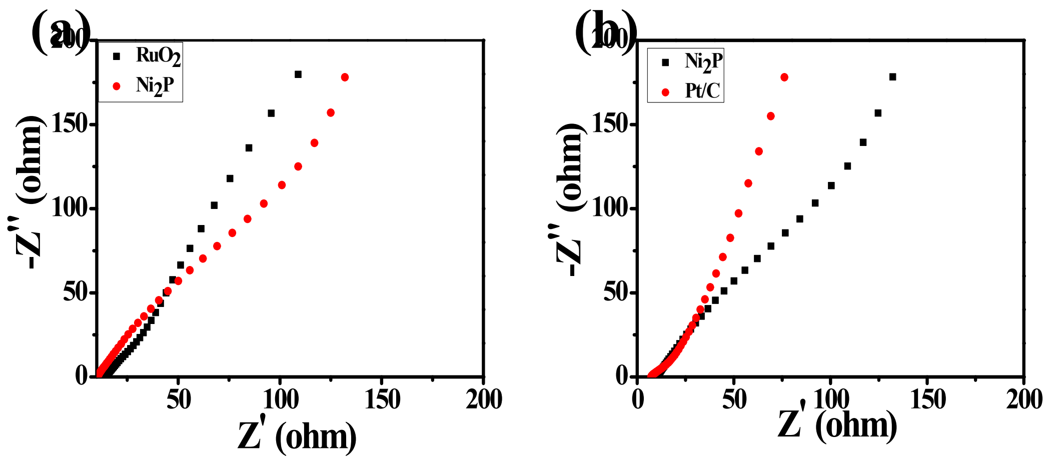

Figure S3. (a) Nyquist Plots of RuO_2 and Ni_2P, (b) Nyquist plots of Ni_2P and Pt/C

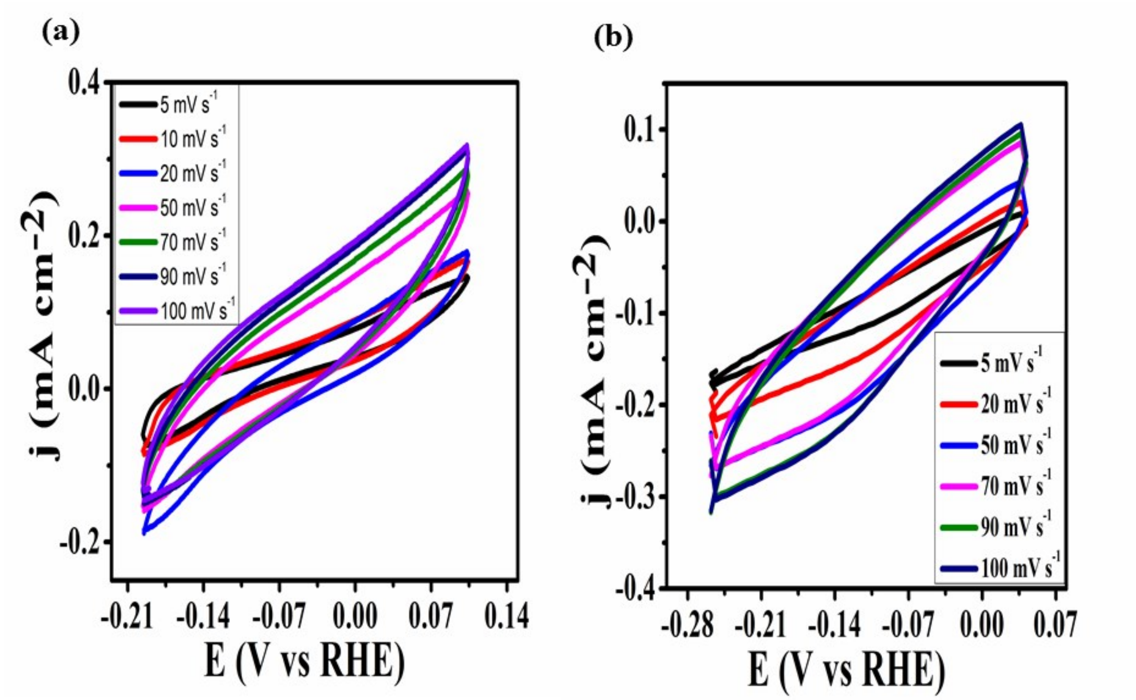

Figure S4. (a, b) Ni_2P CV curves at different scan rates for OER and HER

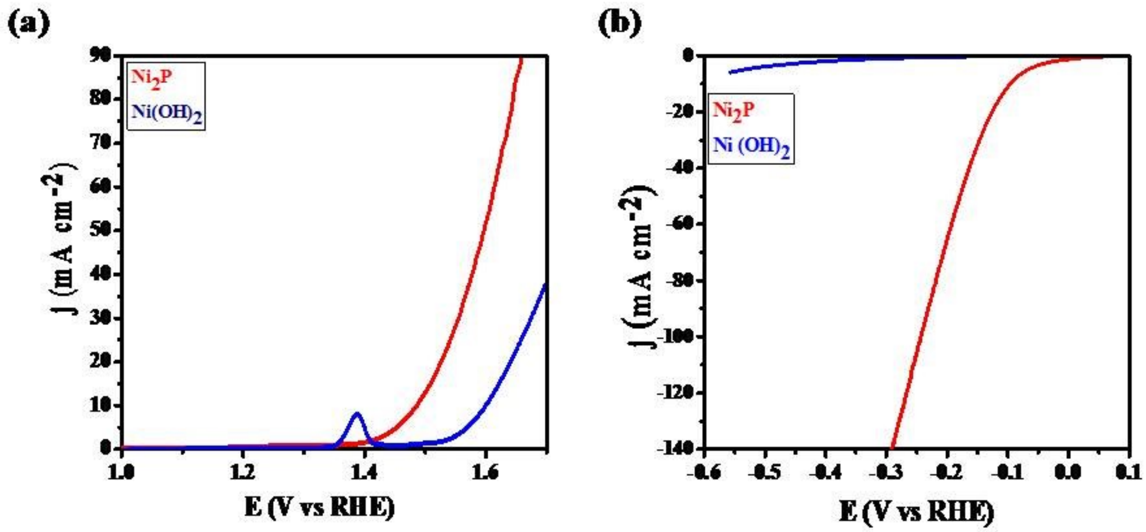

Figure S5. (a) OER polarization curves of Ni $(OH)_2$ and Ni_2P, (b) HER polarization curves of $Ni(OH)_2$ and Ni_2P

$$Ni_3(PO_4)_2 + 3OH^- \rightarrow 2NiPO_4 + NiOOH + H_2O + 3e^- \quad ((a)\text{-}Eq1$$

$$3NiPO_4 + 3e^- \rightarrow Ni_3(PO_4)_2 + PO_4^{3-} \quad ((b) - Eq2)$$

$$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^- \quad ((c) - Eq3)$$

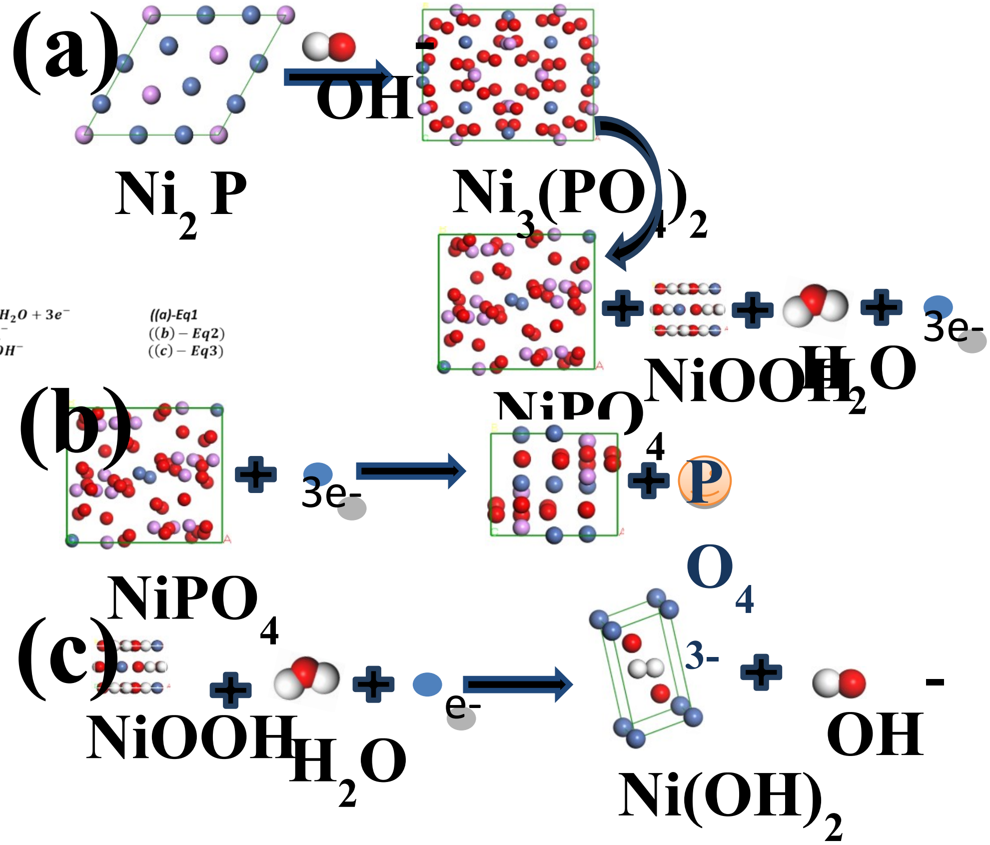

Figure S6. Proposed surface mechanism for OER process on Ni_2P nanosheets.

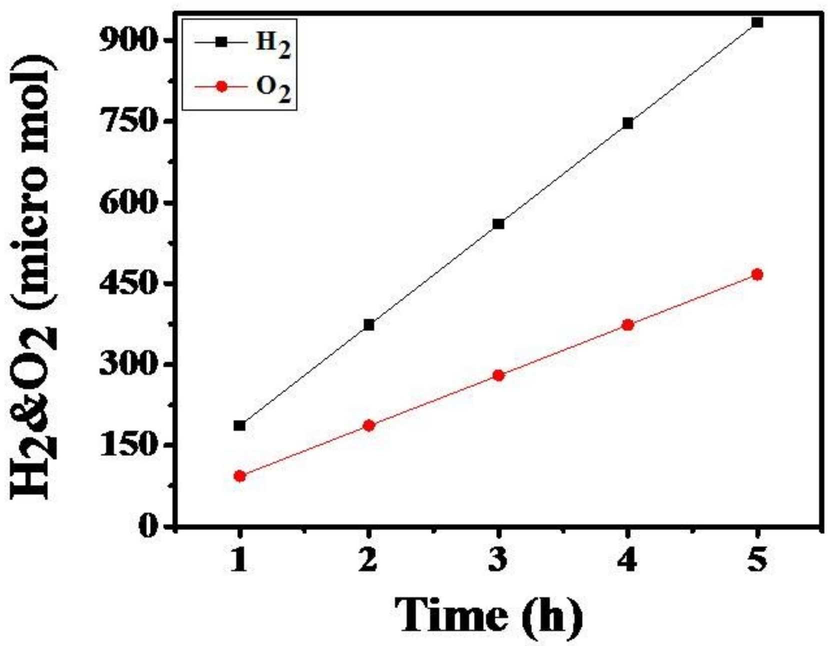

Figure S7. Production of H_2&O_2

Above graph is generated through following calculations.

C= I*t (C= number of coulombs, I= current in amperes and t= time in seconds)

Charge of electron= $1.60*10^{-19}$ coulombs

1 mole of electrons contain= $6.02*10^{23}$ Avogadro's number

1 mole of electrons carry= $1.60*10^{-19}*6.02*10^{23}$= 96485

F= 96485

Now we have

I= 0.01 A & t= 3600 s

Now considering the H_2 producing equation

1 mol of H_2 requires 2 mol of electrons so

Amount of H_2 produced= 3600*0.01/(2*96485) = 186.55 μ mol

Use this equation for different time period and get all calculations.

Table S1. Comparison of the HER performances of Ni_2P with the best-reported nickel phosphide and other reported non-precious HER electrocatalysts.

Catalyst	Morphology	Electrolyte	Over potential (η10)(mV)	Tafel Slope (mV dec^{-1})	Ref.
Ni_2P	Freestanding Porous nanosheets	1M KOH	96	94	This work
Ni_5P_4/C $Ni_{12}P_5/C$ Ni_2P/C	Nanocrystals	0.5M H_2SO_4	103 182 135	51 63 62	[2]
Ni_xP/NF	Nanospheres	1M KOH	63	55	[3]
$Ni\text{-}Ni_xP/CC$	Nanospheres	0.5M H_2SO_4	164	76	[4]
Ni_2P	Nanoparticles	0.5M H_2SO_4	102	46	[5]
CoS_x	Freestanding sheets	1M KOH	127	123	[6]
Ni_3S_2	Nanosheet/NF	1M KOH	223	-	[7]
Ni_3S_2	Nanoparticles/CNTs	1M KOH	480	102	[8]
$Ni_{0.33}Co_{0.67}S_2/Ti$	Nanowires	1M KOH	88	118	[9]

foil					
$NiSe_2$	Nanosheets	1M KOH	184	184	[10]
Co_9S_8@MoS_2	Octahedrons/CNFs	1M KOH	190	110	[11]
CoP	Nanowires/CC	1M KOH	110	129	[12]
CoP	Film	1M KOH	94	42	[13]
CoN_x/C	NPs/Porous carbon	1M KOH	170	75	[14]
MoS_2-Ni_3S_2	Nanorods/NF	1M KOH	98	61	[15]
NiP	Nanoplates	1M KOH	160 (20 mA cm^{-2})	107	[16]
NiMnCoS@rGO	Nanoparticles@sheets	1M KOH	150	52	[17]
Co@N-C	Nanoparticles	1M KOH	210	108	[18]
Co-Ni@NC	Nanospheres	1M KOH	180	193	[19]
CoO_x@CN	Nanoparticles@sheets	1M KOH	232	115	[20]
CoPs	Nanoplates/CFP	0.5M H_2SO_4	48	56	[21]
MoS_2/$CoSe_2$	Nanosheets/nanobelts	0.5M H_2SO_4	68	39	[22]
MoS_2	Film	0.5M H_2SO_4	260	50	[23]
WS_2	Nanosheets	0.5M H_2SO_4	250	60	[24]
Ni-$CoSe_2$	NPs-nanobelts	0.5M H_2SO_4	90	39	[25]
MoS_2@rGO@Mo	Nanosheet	1 M KOH	123	62	[26]
CoO/MoO_x	Nanorods	1 M KOH	40	44	[27]
Ni/NiO	Nanosheet	1 M KOH	110	43	[28]
FeP	Nanoparticles	0.5M H_2SO_4	147	65	[29]
$FeNi_3$/$FeNiO_x$	Nanosheet	1 M KOH	170		[30]
NiCo/$NiCoO_x$	nanowire	1 M KOH	155	80	[31]
Co_xP	Nanoparticles	0.5M H_2SO_4	110	58	[32]
Co_xP	Nanocatalyst	0.5M H_2SO_4	144	58	[33]
$MnMoO_4$	Nanosheet	1 M KOH	179	56	[34]
Co/Co_3O_4	Nanosheet	1 M KOH	90	44	[35]

Table S2. Comparison of the OER performances of Ni_2P with the best-reported nickel phosphide and other reported non-precious OER electrocatalysts.

Catalyst	Morphology	Electrolyte	Over potential (η10) mV	TafelSlope (mV dec^{-1})	Ref.
Ni_2P	Freestanding porous nanosheets	1M KOH	255	57	This work
$Ni_2P_4O_{12}$	Nanocrystals	1M KOH	270	-	
NiP	Hollow dendritic arcitucture	1M KOh	303 920 (20 mA cm^{-2})	67.3	[36]
NiO@NiP	Nanosheet	1M KOH	292	123	[37]
CoP	Film	1M KOH	345	47	[38]
Fe doped Ni_2P	Nanosheet	1M KOH	257	96	[39]
$CuCo_2S_4$	Nanosheet	1M KOH	310	86	[40]
$C@CoP_2$	Nanostructure coreshell	1M KOH	234	63.8	[4]
CoS	Nanosheet	1M KOH	312	-	[41]
Co_9S_8	Nanosheets	1M KOH	288	79	[42]
$CuCo_2S_4$	Nanosheets	1M KOH	310	86	[38]
$Zn_{0.76}Co_{0.24}S/CoS_2$	Nanowires	1M KOH	>316	79	[41]
$Co_9S_8@MoS_2$	Octahedrons/CNFs	1M KOH	430	61	[9]
NiFeLDH	Nanoplates	1M KOH	302	40	[42]
CoMnLDH	Nanoplates	1M KOH	324	43	[43]
$Co_5MnLDH/MWCNT$	Nanosheets/MWCNT	1M KOH	300	73.6	[44]
NiMnCoS@rGO	Nanoparticles@sheets	1M KOH	249	66	[15]
$(Ni,Co)_{0.85}Se@CC$	Nanotubes@CC	1M KOH	255	79	[45]
CoCrLDH	Nanosheet	1M KOH	340	81	[46]

Ni $(OH)_2$	Nanosheet/NF	1M KOH	170	150	[47]
$Zn_{4-x}Co_xSO_4$ $(OH)_6.0.5H_2O$	Nanoplates	0.5M KOH	370	60	[48]
NiP	Nanoplates	1M KOH	320	72.2	[14]
NiMnCoS@rGO	Nanoparticles@sheets	1M KOH	320	53	[15]

Table S3. Comparison of overall water splitting performances of $Ni_2P||Ni_2P$ with the best reported bi-functional electrocatalysts in the basic electrolyte.

Cathode catalyst	Anode catalyst	Electrolyte	HER Over potential (η10) mV	OER Over potential (η10) mV	E at j= 10 mA cm^{-2} (V)	Ref
Ni_2P	Ni_2P	1M KOH	96	255	1.47	This work
CoS_x	Co_9S_8	1M KOH	127	288	1.55 (20 mA cm^{-2})	[7]
Ni_xP_y	Ni_xP_y	1M KOH	160 (20 mA cm^{-2})	370	1.57	[48]
NiS	Ni_2P	1M KOH	126	265 (20 mA cm^{-2})	1.67	[14]
$Ni(OH)_2$/NF	$Ni(OH)_2$/NF	1M KOH	178 (20 mA cm^{-2})	330 (50 mA cm^{-2})	1.68	[47]
NiS/NF	Ni/NF	1M KOH	158 (20 mA cm^{-2})	355 (50 mA cm^{-2})	1.67	[49]
Ni_2P/Ni/F	Ni_2P/Ni/NF	1M KOH	90	200	1.49	[50]
NiMnCoS @rGO	NiMnCoS@r GO	1M KOH	150	320	1.56 (20 mA cm^{-2})	[51]
Co-S/CTs/CP	Co-S/CTs/CP	1M KOH	190	307	1.74	[52]

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